Science Progress.

No. 5. JULY, 1894. Vol. I.

IONIC VELOCITIES.

IF a current of electricity be passed through the solution of a metallic salt, decomposition generally occurs, and the products appear at the electrodes where the current enters and leaves the liquid. Since the intervening solution is unaltered, we must suppose that a continual passage of the parts of the salt in opposite directions is going on, the molecules being split up and reformed as their constituent atoms change partners. The atoms thus travel through the solution, and are hence called "ions"—kations or anions as they travel with or against the current. Thus in a solution of hydrochloric acid the hydrogen travels with the current and appears at the kathode, while the chlorine moves in the opposite direction and is set free at the anode. An account of the investigations which have been made on this motion of the ions, and on the velocities with which they travel, is the subject of this article.

We must first consider whether it is possible to calculate these velocities from the electrical properties of solutions. Faraday discovered that the passage of a definite quantity of electricity liberated a mass of a certain element which was proportional to the chemical combining weight of that element —not to its atomic weight, but to its atomic weight divided by its valency. Thus the passage of one unit (on the centimetre-gram-second system) of electricity liberated 0·0001035 gram of hydrogen, and 0·0001035 × 35·4 gram of chlorine from a solution of hydrochloric acid or 0·0001035 × 108 gram of

silver from a solution of silver nitrate. When it is remembered that the mass of the atom of hydrogen is to that of silver as 1 : 108, it is evident that the same quantity of electricity always passes when one univalent atom is set free. In the case of divalent atoms like oxygen, we find that one unit of electricity liberates $0{\cdot}0001035 \times \frac{\text{Atomic Weight}}{2}$ grams, hence the quantity of electricity which is needed to liberate one divalent atom is twice as great as that required to set free one univalent atom. This definite relation between the quantity of electricity passing through the solution, and the number of atoms liberated, is easily represented by supposing that each univalent atom, while it is travelling through the solution as an ion, carries a definite charge of electricity—of positive electricity if it is a kation, of negative electricity if an anion—which it gives up to the electrode when it is reached, while each divalent ion carries twice as much, and so on. The passage of a current through a solution can therefore be looked upon as a kind of convection. A constant stream of kations carries positive electricity in one direction, and a corresponding stream of anions carries negative in the other.

Suppose we have N gram-equivalents of salt, and consequently N gram-equivalents of both anion and kation, in each cubic centimetre of the solution. If the velocity of the anion be v and that of the kation u, the numbers of them passing in one second across each square centimetre of area in a plane at right angles to the direction of their motion are Nv and Nu respectively, so that the quantity of salt decomposed per second is $N(u + v)$ or NV gram-equivalents where V is the relative velocity of the ions past each other. Now by Faraday's law we know the quantity of electricity which passes when one gram-equivalent of salt is decomposed: it is $\frac{1}{0{\cdot}0001035}$ units. The quantity of electricity which passes in one second through unit area of cross section of the solution at right angles to the flow is therefore $\frac{NV}{0{\cdot}0001035}$ units. But this gives the strength of the

current through this same area, and if we take Ohm's law we can find another measure for it, *viz.*, the electromotive force between the sides of a centimetre cube divided by its electrical resistance. If we call these E and r respectively, we get—

$$\frac{E}{r} = \frac{NV}{0{\cdot}0001035}$$

$$\therefore V = 0{\cdot}0001035 \times \frac{E}{Nr}.$$

Now since the length of the side of our little cube is 1 centimetre, E represents the fall of potential (*i.e.*, the electromotive force) per unit length. If we put E = 1 we shall get a value for V corresponding to what we may call unit potential gradient—

$$V_1 = \frac{0{\cdot}0001035}{Nr} \quad \ldots\ldots \text{(i.)}$$

r, the resistance of our little cube is the specific resistance of the solution, and can be measured by a modification of the ordinary Wheatstone's bridge method. We can, therefore, at once deduce the value of V_1, the velocity with which the ions are *sheared past each other* by a potential gradient equal to unity. Thus in the case of a solution of hydrochloric acid whose strength is one-tenth of a gram-equivalent (3·64 grams) per litre (*i.e.*, a decinormal solution), the specific resistance was found by Kohlrausch to be $2{\cdot}90 \times 10^{10}$ in C.G.S. units. N the number of gram-equivalents per *cubic centimetre* is 10^{-4}, hence—

$$V_1 = \frac{0{\cdot}0001035^2}{10^{-4} \times 2{\cdot}90 \times 10^{10}} = 3{\cdot}57 \times 10^{-11}$$

centimetres per second.

This is calculated for unit potential gradient on the C.G.S. system. For a gradient of one volt per centimetre we get $V = 3{\cdot}57 \times 10^{-3}$ or ·00357 centimetres per second.

In order to find the absolute velocity of either hydrogen or chlorine, we must consider whether the opposite ions travel with equal velocity. If that were so the absolute velocity of each would obviously be half their relative

velocity past each other. Consider what will occur if they move with unequal speeds. Suppose that the anions move faster than the kations. In that portion of the solution which surrounds the anode, ions will arrive faster than in the portion surrounding the kathode, while those leaving it leave more slowly. Hence the strength of the solution near the anode will become greater than that of the solution near the kathode. In the case of an electrolytic cell with platinum electrodes, in which the quantity of salt in solution continually diminishes, this implies that more of the salt decomposed will come from the neighbourhood of the kathode than from the neighbourhood of the anode, and that the quantities of salt taken from the solutions near the anode and kathode, respectively, are in the ratio of the velocity of the kation to the velocity of the anion.

In nearly every case phenomena of this kind are actually found to occur. Thus, if an electrolytic cell, with platinum electrodes, containing a solution of hydrochloric acid, is divided into three portions by partitions of porous earthenware, when the current is passed no change occurs in the central division, but the strength of solution in the divisions containing the electrodes becomes less—the anode division losing its contents much faster than the kathode division. From this observation Hittorf concluded by the reasoning given above that the hydrogen travelled faster than the chlorine. He described the phenomenon as the "Migrations of the ions". Let us, for example, take the case of a solution whose strength is one-tenth of a gram-equivalent of hydrochloric acid (3·64 grams) per litre. We should find that when such a solution is electrolysed, out of each gram of HCl decomposed, ·21 gram was taken from the anode solution, and ·79 gram from the kathode solution. The ratio of the velocities of the hydrogen and chlorine ions must therefore be as 79 : 21.

Now the *relative* velocity of the ions past each other is the sum of the opposite *absolute* velocities. We have, therefore, only to divide the relative velocity, ·00357 centimetres per second, into two parts, in the ratio 79 : 21, in order to find that in a decinormal solution of hydrochloric

acid, when the potential gradient is one volt per centimetre, the hydrogen ion travels with a velocity of ·00282 centimetres per second, and the chlorine ion with a velocity of ·00075 centimetres per second. F. Kohlrausch (*Wiedemann's Annalen*, vols. vi., xxvi. and l.) has made a long series of determinations of the conductivity (*i.e.*, the reciprocal of the specific resistance) of solutions, and used the numbers obtained to calculate the ionic velocities. He expresses his results in terms of "molecular conductivity"—*i.e.*, conductivity (k) divided by strength of solution in gram-equivalents per litre (m). This corresponds to $\frac{1}{1000Nr}$ in our equation (i.) (since N is the concentration referred to cubic centimetres), so that we get

$$V = u + v = \frac{0{\cdot}0001035}{Nr} = 0{\cdot}1035 \times \frac{k}{m}. \quad \ldots \text{(ii.)}$$

He finds that as the solutions become more dilute, the molecular conductivities, and, therefore, the velocities of the ions, in general increase, but that in most cases they come to a limit which enables him to determine either by exterpolating in a formula, or by drawing a curve, the value of the velocity corresponding to infinite dilution. Thus the most recent values for sodium and lithium chlorides (*Wied. Ann.*, 1893, l. 7, 403) are the following, where u is the velocity of the kation, and v that of the anion, each in 10^{-6} centimetres per second, while m is the concentration in gram-equivalents per litre :—

	Na Cl			Li Cl		
m	$u+v$	u	v	$u+v$	u	v
5	438	153	285	334	80	254
1	765	278	487	651	169	482
0·1	952	360	592	853	259	594
0·01	1059	415	644	962	318	644
0·001	1110	440	670	1013	343	670
0·0001	1129	448	681	1037	356	681
∴ 0	1140	450	690	1050	360	690

The numbers obtained for the same ion in various salts are found to differ while the solutions are strong, but to approach as dilution goes on, and finally to become identical when the limit is reached. This is clearly shown by the preceding table in the case of chlorine, the values for which in sodium and lithium chlorides are given in the columns under the heading *v*. Kohlrausch was thus enabled to assign to each ion a *specific* ionic velocity, which, when the dilution is infinite, is independent of the nature of the other ion or ions present. The following are some of his latest values :—

$K = 66 \times 10^{-5}$ cms. per sec.		$Cl = 69 \times 10^{-5}$ cms. per sec.	
$Na = 45$	,, ,,	$I = 69$	,, ,,
$Li = 36$	,, ,,	$NO_3 = 64$	,, ,,
$NH_4 = 66$	,, ,,	$OH = 182$	,, ,,
$H = 320$	,, ,,	$C_2H_3O_2 = 36$	,, ,,
$Ag = 57$	,, ,,	$C_3H_5O_2 = 33$	,, ,,

These numbers are calculated for a potential gradient of one volt per centimetre and a temperature of 18°C.

It is interesting to observe the magnitude of the forces required to drive the ions with a certain velocity. If we have a potential gradient of one volt per centimetre, the electric force is 10^8 in C.G.S. units. The charge of electricity on one gram-equivalent of any ion is $1/{\cdot}0001035 = 9653$ units, hence the mechanical force acting on this mass is 9653×10^8 dynes. This produces (suppose) a velocity u, then the force required to produce unit velocity is $P_A = \frac{9{\cdot}653 \times 10^{11}}{u}$ dynes $= \frac{9{\cdot}84 \times 10^5}{u}$ kilogram weights. If the ion have an equivalent weight A, the force producing unit velocity when acting on one gram is $P_1 = 9{\cdot}84 \times 10^5 \times \frac{1}{Au}$ kilogram weights.

In the case of potassium this gives to the force acting on one gram in very dilute solution a value equal to the weight of 38,000,000 kilograms. Since the velocity is uniform it follows that the frictional forces are equal and opposite to this, and collecting all such opposing forces under the name

of "electrical friction," Kohlrausch gives a table of coefficients at a temperature of 18° C., from which the following numbers are taken :—

	P_A	P_1		P_A	P_1
K	150×10^7	$3{\cdot}8 \times 10^7$	Cl	140×10^7	$4{\cdot}0 \times 10^7$
Na	220	9·5	I	140	1·1
Li	270	39·0	NO_3	150	2·5
NH_4	150	8·3	OH	54	3·2
H	31	31·0	$C_2H_3O_2$	270	4·6
Ag	170	1·6	$C_3H_5O_2$	300	4·1

From a list of ionic velocities, such as that given on the opposite page, the conductivity of any salt solution can be calculated by taking the sum of the opposite velocities of its ions, and the result compared with observation.

This comparison would be difficult at very great dilution, so Kohlrausch took solutions of one-tenth of a gram-equivalent per litre, when in general the velocities are approaching their limiting value. He gives a table of twenty-five electrolytes, the numbers for which all agree well with observation (*Wied. Ann.*, xxvi., p. 215). The following are fair examples—the numbers being reduced to C.G.S. units :—

Name of Salt.	Molecular conductivity calculated from the ionic velocities.	Molecular conductivity observed.[1]
KCl	112	111
$NaCl$	91	92
$LiCl$	82	82
KI	114	114
HNO_3	340	343
$\frac{1}{2}BaCl_2$	90	92
$\frac{1}{2}ZnCl_2$	83	82
$NaOH$	187	182

In the case of substances whose molecular conductivity varies greatly between a strength of one-tenth gram-equivalent per litre, and infinite dilution, the effect of concentration is so great that no agreement is obtained; thus acetic

[1] The latest numbers are rather greater than these, but the differences affect both observed and calculated results equally, so the comparison is the same.

acid should give 316·8, while the observed number is 4·6 for the strength given above, and only rises to 138·6 for a strength of one hundred thousandth of a gram-equivalent per litre.

The first direct measurement of the velocity of an ion under a definite potential gradient was made by Oliver Lodge (*British Association Report*, 1886). A glass tube contained a jelly in which sodium chloride was dissolved with just enough caustic soda to make it alkaline and bring out the colour of a little phenol-phthallein, which was added. The tube ended in two vessels filled with dilute solutions of sulphuric acid. A current of electricity was then passed from one vessel to the other along the tube. The hydrogen ions of the sulphuric acid travel with the current, and when they enter the tube displace the sodium ions, which are also moving in the same direction, and form hydrochloric acid. The presence of this acid decolourises the phenol-phthallein and thus the movement of the hydrogen along the tube can be traced. Lodge found that the velocity produced by a potential gradient of one volt per centimetre came out from three experiments, as ·0029, ·0026 and ·0024 centimetres per second respectively. If this be compared with the number (·00282) calculated on p. 377, for a decinormal solution, or with Kohlrausch's value, ·0032 for infinite dilution, it will at once be seen how remarkable the agreement is, and what strong evidence it gives for the truth of the theory.

Some further experiments, in which the motion of barium and chlorine ions were traced by the precipitates produced by contact with sulphuric acid, did not give such good results, but the disturbances produced by the precipitates, and the uncertainty of potential gradient introduced by the varying resistance of the solution at the places where they are formed, are quite enough to explain the discrepancy.

The present writer has determined the velocities of a few other ions by a method which gets over some of the difficulties inherent in the use of indicators or precipitates (*Philosophical Transactions of the Royal Society*, 1893, A, p. 337). A pair of solutions, with one ion in common, is used, one at least of which is coloured. The solutions must be of the same equivalent strength, nearly equal specific

resistance, and of slightly different density, such for instance as decinormal solutions of copper and ammonium chlorides with enough ammonia added to each to bring out the deep blue colour of the copper. The ammonium chloride solution is rather lighter than the other and can be gently poured on to its surface, so that a fairly sharp line of junction is obtained in a vertical tube. When a current is passed across this junction it carries the copper and ammonium ions forward with it, while the chlorine ions in both solutions move in the opposite direction. Since the blue colour depends on the presence of the copper ion, the boundary between the colours moves with the current and its speed can be measured. It was proved by observation that the speed is proportional to the potential gradient, and hence the specific ionic velocity for unit gradient can be deduced. For copper it came out ·000309. For infinite dilution Kohlrausch gives ·00031, but this is not strictly comparable. It is a little difficult to get a value from theory for the strength of solution used for this experiment, as no migration data for copper chloride are known, but the number is certainly less than ·00030. The motion of an acid radicle was investigated by using solutions of potassium bichromate and potassium carbonate. The ionic velocity of the bichromic acid group (Cr_2O_7) was found to be ·00047, ·00048, and ·00046 by three experiments. From the conductivity and migration data the number ·000473 can be calculated from Kohlrausch's theory. The method was then extended to the case of alcohol solutions, and measurements were made with solutions of cobalt nitrate (red) and cobalt chloride (blue). The agreement with theory was again fairly close.

Further experiments are now being made ; the behaviour of solutions in agar jelly is under investigation, and it is hoped that measurements will be obtained in the case of solutions of abnormally low conductivity, such as those of ammonia and acetic acid.

It seems certain then that Kohlrausch's theory of ionic velocity represents the truth, at all events in the case of good electrolytes in dilute solution. Let us consider what happens when the concentration is greater and the

molecular conductivity becomes less. The work of the founders of the "Dissociation" theory has at all events convinced us that in such cases a part only of the salt present is actively concerned in conveying the current, whatever be the physical cause of the inactivity of the rest. We are thus prevented from supposing simply that the ionic velocities are reduced by the increased viscosity of the solution—an idea which an examination of viscosity data would also upset. We must take a dynamical view of the ionisation equilibrium and (using for the sake of convenience the language of the dissociation theory) imagine each ion sometimes free and therefore active, and sometimes combined with an opposite ion and rendered inert. The ratio of the time during which each ion is on the average free, to the time during which it is combined, measures, as will at once be seen, the fractional number of the molecules which are at any instant dissociated. While it is free each ion is urged forward by the electric forces with a velocity equal to its specific velocity at infinite dilution (except for a small charge introduced by the increased viscosity). While it is combined it is at rest. We thus get an *average* velocity which is reduced to the value required on Kohlrausch's theory by the diminished molecular conductivity.

The process of electrolysis in strong solutions of those salts which have a low conductivity, and are therefore only slightly "dissociated," is probably in reality a rather complicated phenomenon. In order to explain the abnormal migration constant of Cadmium iodide in alcohol, observed by Hittorf, the idea of complex ions has been introduced. In the case of this electrolyte, more salt is taken from the solution round the kathode than is decomposed, so that the anode solution actually gets stronger. This is explained by supposing that the ions in this case are Cd and $I_2(CdI_2)$, a molecule of undecomposed salt being attached to the anion.

While measurements were being made with the solutions of cobalt chloride and cobalt nitrate in alcohol mentioned above, it was found that good results could only be obtained with solutions whose strength was less than about 0·06 gram-equivalent per litre. In the case of stronger solutions vari-

ous curious phenomena (analogous to those observed by Gore, *Proc. R. S.*, 1880 and 1881) were observed. Several surfaces of separation often appeared, the liquid between them being of various tints, ranging from red through purple to blue, and occasionally some of these junctions had their motion reversed, and either for a time or permanently travelled in the wrong direction.

This again favours the view that in such solutions complex ions are formed. Whether any such phenomena occur in the case of aqueous solutions is not yet clear, but experiments in the velocities of the ions of electrolytes of abnormally low conductivity may throw light on this question.

It will be observed that nothing has been said about the state in which the ions exist or the mechanism by which they pass from place to place. The theory and its confirmation are thus quite independent of the view we may take of the nature of the processes of solution and electrolysis. The phenomena of chemical action and the agreement with Ohm's law shown by electrolytes prove that a continual molecular interchange of partners is going on whether or not the current passes, but a knowledge of the particular mechanism by which this is accomplished is not necessary for the investigation of Kohlrausch's theory. Whether we accept the view of Van t'Hoff, Ostwald, and Arrhenius, which supposes that all but a small percentage of the number of molecules in an electrolytic solution are dissociated into ions existing uncombined in the liquid, or the chemical hypothesis which requires freedom only at the instant of interchange of partners between two colliding molecular structures, we are obliged to imagine the ions travelling by some means under the influence of the electric forces and attaining a definite average limiting velocity. But although Kohlrausch's theory does not *oblige* us to accept either the "dissociation" or the "chemical" view of electrolysis, the fact that in dilute solution each ion has a definite velocity independent of the other present seems to *favour* the idea that electrolytes contain free ions. It is important to remember that, as J. J. Thomson has pointed out (*Phil. Mag.*, 1893, xxxvi., p. 320), two bodies charged with opposite kinds

of electricity have their attraction very much diminished when they are immersed in a medium of high specific inductive capacity like water. It follows from this that when, during the changes and chances of their molecular life, two ions come in very close contact with particles of solvent, their mutual attraction may be less than the attraction between one or both of them and the surrounding medium, and dissociation may take place. This force attracting a charged ion to the solvent, which is of the same nature as that between a charged body and a non-electrified conductor near it, will prevent its combining with an opposite ion until one happens to get so close that the other forces are overcome. This will of course occur less frequently as the number of ions gets less, and so in very dilute solutions the dissociation remains almost complete. It is not necessary to assume that the ion remains always in combination with the same molecules of water, which would involve a transference of solvent under the action of the electric forces. In the jostling crowd of solvent molecules it is soon passed on to others, and so works its way towards its destined pole. As long as it meets few distractions, in the shape of ions of opposite kind, on the road, its speed depends only on itself, the solvent and the electric forces, but when such encounters become frequent it sometimes forms connections which, while they last, render the ion inactive, and totally prevent the performance of its proper electrolytic work. This loose combination with the solvent would give the ions freedom to travel, without allowing them to wander about under what some consider the insufficient chaperonage of their own electric charges.

The fact that water, which has a high specific inductive capacity, makes such a good electrolytic solvent is of great interest. The power which a liquid has of enabling substances dissolved in it to carry electricity may be largely due to the reduction which it causes in the electric forces holding their molecules together, and the consequent increased facility for the production and preservation of dissociated ions. This property would depend on the specific inductive capacity, and it therefore becomes most interesting

to compare the values of this dielectric constant for various liquids with the conductivities of salts dissolved in them. Since for our purpose a comparison with a definite constant of the pure solvent is needed, the ratio of the conductivities of very dilute solutions should be used. The conductivities of very dilute solutions of calcium chloride in methyl and ethyl alcohols have lately been determined by Fitzpatrick and the writer of this article. There are not for these cases such definite limiting values as for water solutions, but the following relative numbers for the molecular conductivities (that of the infinitely dilute aqueous solution being taken as 100) correspond to the greatest dilutions reached :—

Water 100. Methyl Alcohol 70. Ethyl Alcohol 23.

Although the specific inductive capacities of water and ethyl alcohol have been measured by several observers, the only value for methyl alcohol is that given by Tereschin, so for the sake of comparison his results for all three are used. He gives water = 83·7 ; methyl alcohol = 32·65 ; ethyl alcohol = 25·8. These numbers must be corrected for the viscosities of the liquids (the relative values of which are 100 : 63 : 120). If we assume that the ionic velocities, and therefore the conductivities, are inversely proportional to the viscosities we get the following values :—

Water 100. Methyl Alcohol 63. Ethyl Alcohol 26.

The approximation of these numbers to those given above for the conductivities, suggest that these properties are at all events the chief factors in determining the "relative ionisation power" of a solvent.

If the table of velocities on p. 377 be examined, it will be seen that the values for the elements in a chemical group, such as that of the alkali metals, increase with the atomic weight. Thus we get L*i* = 36, N*a* = 45, K = 66. Studies of these relations have been made by Ostwald, Walden and others, and G. Bredig has collected all known results and added others from his own observations in an elaborate paper in the *Zeitschrift für Physikalische Chemie*, 1894, xiii., p. 243. The ionic velocity, like so many other physical and chemical properties, appears to be a periodic function of the atomic weight of the elements, and if plotted on a

curve shows maxima and minima, similar elements falling on the corresponding points of each portion of the curve.

The conductivities of an immense number of salts containing one or more organic radicles have also been measured and the velocities of their ions calculated. The following are some of Ostwald's results :—

Univalent Anions.				Difference for addition of CH_2.
Formic acid group		HCO_2'	51·2	
				- 12·9
Acetic	,,	$H_3C_2O_2'$	38·3	
				- 4·0
Propionic	,,	$H_5C_3O_2'$	34·3	
				- 3·5
Butyric	,,	$H_7C_4O_2'$	30·8	
				- 2·0
Valeric	,,	$H_9C_5O_2$	28·8	
				- 1·4
Caproic	,,	$H_{11}C_6O_2$	27·4	

Similar tables for univalent kations of the ammonium, methylammonium, etc., series follow, and an immense amount of similar matter will be found in Bredig's paper. The differences for successive additions of CH_2 decrease as we ascend the series; the ionic velocity is hence described as a "Convergent additive property". In general, as it is natural to expect, compound ions travel more slowly than elementary ones, but no very simple relations can be traced, as the nature as well as the number of the compounded atoms exerts an important influence on the velocity.

The speed with which an ion travels in solution, however, so obviously depends on many factors, that one would only expect a qualitative relation between it and the constitution of the ion.

The extension of Kohlrausch's theory to solvents other than water, a first attempt at which is described above, and the investigation of aqueous solutions of abnormally low conductivity, seem the most promising fields for future work. Most interesting information about the existence and nature of complex ions ought to be thus obtained and light thrown on the whole subject of solution and electrolysis, for it is by the study of apparent exceptions that we learn the full scope and limitations of a new theory.

W. C. Dampier Whetham.

INSULAR FLORAS.

PART II.

BOTANICAL enterprise in New Zealand is very active, owing doubtless to the fact that very early in the settlement of the country by Europeans the community had a good foundation on which to build a superstructure; and this may be said of Australia. Even now there are better general works, of moderate cost, on the botany of our colonies at the Antipodes than on the European flora. Allan Cunningham should not be forgotten in the history of botanical discovery in New Zealand; but the botanical results of Sir James Ross's Antarctic expedition by Sir J. D. Hooker, is the foundation to which I allude. On this basis the colonists have not only worked out the details of the botany of the main islands, but almost all of the outlying small islands, such as the Snares, Auckland, Campbell, Macquarie, Antipodes, Bounty and Kermadecs, have been visited and almost thoroughly explored. But I will first take the main islands, though I do not propose entering into much detail concerning their flora, because the subject has been discussed over and over again. Since the publication of Sir Joseph Hooker's *Handbook* in 1864, no complete account of the flora, so far as it is known, has appeared, though one has long been promised and expected. In the meantime an enormous number of proposed new species have been described; that is to say, an enormous number in proportion to the whole. Hooker's *Handbook* contains descriptions of 935 species of flowering plants belonging to 302 genera; and since the publication of that work descriptions of about 540 reputed new species have appeared in the *Transactions of the New Zealand Institute*, to say nothing of those published elsewhere. A large number of them are distinct and well-defined species. On the other hand, more than half of them, probably, would not be accepted by the majority of botanists. With the exception of one very interesting new genus, to be referred to again, they all belong to previously known genera; and such

familiar and widely-spread genera as *Ranunculus*, *Senecio*, *Veronica* and *Carex* yield, between them, nearly 100 of these new species. Among the Australasian genera *Coprosma* and *Olearia* are credited with fifty between them; and *Carmichælia*, *Celmisia* and *Astelia* with about a dozen each. It is evident, therefore, disregarding the limitation of species, that the later discoveries in New Zealand in no way affect the previous problems of distribution. As already indicated in a previous article, recent explorations have revealed the existence of exceedingly few extensions of New Zealand types, specific or generic, so that the strongly endemic character of the flora is still maintained; but the very close affinity of the orchid flora of New Zealand with that of Australia has been strengthened by the discovery in New Zealand of *Caleana minor*, *Calochilus campestris* and *Calochilus paludosus:* the first a native of New South Wales and Tasmania; the second the same and extending to Queensland; and the third New South Wales and Queensland. Why this close relationship should exist, is difficult to explain, in the absence of the more prominent, more universal and more easily dispersed Australian types, especially when we consider that nearly the whole of the northern island of New Zealand is in a lower latitude than Tasmania. Another fact of interest in this connection is the discovery in Stewart Island, in the extreme south of New Zealand, of two very rare Tasmanian plants in abundance, namely, *Actinotus bellidioides* (Umbelliferæ) and *Liparophyllum Gunnii*, a monotypic genus of the Gentianaceæ. But it is not my intention to discuss the question at this point. The only other fact I have to repeat here is that but one new genus has been discovered since the publication of Hooker's *Handbook* in 1864—at least the only one that has come under my notice. This is a very singular and very small herbaceous plant named *Tetrachondra Hamiltonii* (1), and so like *Tillæa* in habit that it was first referred to that genus. The flowers being very minute, their structure was at first misunderstood. This plant not only closely resembles *Tillæa*, but actually grows in semi-aquatic situations associated with a species of this genus. Its immediate affinity has not been

determined, supposing such exists; but it appears to be an aberrant member of the Boragineæ, with strictly opposite leaves and albuminous seeds.

The smaller islands appertaining to the New Zealand region may be dealt with under two heads, namely, those contiguous to the main islands, and those of a more oceanic character. Space will permit of reference to a very small selection only of those belonging to the former category; but as the accounts of these small floras are exceedingly interesting, it would not be justifiable to pass them over altogether, especially as they appeared in publications accessible to a comparatively small number of persons. Foremost comes Stewart Island (2), South Island of the older books and maps, and still of the Colonial Office list, though not of the colonists, who designate the former Middle Island as South Island. Some explanation is necessary, because much confusion has arisen in consequence of this transfer of names. Stewart Island has an area of about 640 square miles; its highest point is about 3200 feet above sea-level, and it is traversed by the forty-seventh parallel of latitude. In this comparatively high southern latitude a most luxuriant vegetation flourishes, including extensive groves of tree ferns, belonging to five different species; and individual specimens occur up to twenty-five feet in height. In strong contrast to this profuse fern vegetation is the blaze of crimson presented during the months of December and January by the "Rata," *Metrosideros lucida*. Indeed, from Mr. Kirk's description Stewart Island must be a delightful garden of ferns and flowers. But to return to the more scientific aspect of the subject. So far as at present known, and the island has been by no means thoroughly explored, the flora comprises 380 species of flowering plants and nearly 70 species of ferns and lycopods. The fern vegetation is really marvellously rich, and Mr. Kirk gives reasons for supposing that several other species will yet be discovered. I cannot resist referring to his description of the 'Archdeacon's Cove,' where he found *Hymenophyllum pulcherrimum* with fronds between two and three feet long, and *Todea superba* having a stout stem

eighteen inches high with a crown of fronds, the longest five feet in length! I may add that no fewer than twenty species of *Hymenophyllum* and *Trichomanes* have been collected. Epiphytes, apart from ferns, are abundant, including the orchids, *Earina mucronata*, *E. autumnalis* and *Dendrobium Cunninghamii*. Indeed, the climate appears to be exceptionally mild, as the plants of the colder regions, such as the beeches and *Phyllocladus alpinus*, are absent; yet "numerous species usually restricted to alpine or subalpine situations occur at sea-level". This sounds somewhat paradoxical, but this phenomenon is exemplified in other parts of the world, even to some extent in our own islands by the genera *Armeria* and *Plantago*. The flora also includes several apparently endemic species and a few only known elsewhere from the Auckland and Campbell Islands. Finally not a single leguminous plant has hitherto been observed in the island.

The Snares is the name given to a group of small granitic rocky islands, situated about sixty-five miles south of Stewart Island. The largest island is about a mile and a half in its greatest diameter and less than 500 feet in its greatest altitude. This was botanised by Mr. Thos. Kirk in 1890 (3), who collected twenty flowering plants and three ferns, besides four evidently naturalised grasses. The only woody plants are: *Olearia Lyallii*, *Senecio Muelleri* and *Veronica elliptica*. The first, a member of the Compositæ, is the most abundant, and in level situations forms a tree, occasionally nearly thirty feet high with a trunk three feet in diameter. *Senecio Muelleri* attains nearly as large dimensions and is described as a very noble species. It was originally discovered on Herekopere Island, one of the small islands adjacent to Stewart Island, and it has also been recorded from South Cape Island; but it is not known to inhabit any other locality. No doubt, as Mr. Kirk suggests, the herbaceous vegetation is so meagre in consequence of the excessive number of penguins, gulls and other birds, which trample small plants out of existence. A vigorous grass-like *Poa foliosa* flourishes all the more luxuriantly for the presence of the birds, and the same may

be said of the large-leaved *Aralia Lyallii*, which has large orbicular leaves two feet in diameter, borne on stout petioles. The only endemic plant is *Ligusticum acutifolium*, observed only in one place.

Passing from the extreme south of New Zealand to the extreme north there is a group of islands called the Three Kings; the larger ones known as the Great King, East King and West King respectively. They are situated about thirty-eight miles north-west of Cape Maria van Diemen. The largest of these islands is less than two miles in its greatest diameter, and barely a thousand feet high; and the others are much smaller; yet botanically they are exceedingly interesting. Previous to 1887, however, they had not been visited by a botanist. In the spring of that year, and again in 1889, Mr. T. F. Cheeseman was given a passage on the Colonial Government steamer which periodically visits the outlying islands to rescue possible shipwrecked sailors; and he has published a full account of these visits (4). On the first occasion they landed only on the Great King, where they collected eighty-two species of vascular plants including fifteen ferns. Three are described as new, namely, *Pittosporum Fairchildii*, *Coprosma macrocarpa* and *Paratrophis Smithii*. On the second occasion the party succeeded in landing on the West King as well as on the Great King, and on the former a notable discovery was made by the botanist, who, to his great delight, found that the whole of the northern slope, where not too steep, was covered with the rare *Meryta Sinclairii* (*Botryodendron Sinclairii*), a very striking, large-leaved araliaceous tree. Interspersed with it, in the more sheltered places, were some fine luxuriant specimens of *Cordyline australis*, with an undergrowth of the broad-leaved form of *Piper excelsum*. Until this discovery was made it was believed that the *Meryta* was almost extinct. It had never been found on the mainland, except under cultivation, and only a few trees were known to exist in the Taranga Islands (Hen and Chickens), some 200 miles distant down the eastern coast, off the mouth of Wangari Harbour, "where it is likely soon to become extinct". The second visit brought the total number

of vascular plants up to 143. This is a comparatively small flora; but, as Mr. Cheeseman points out, it is in no danger of being destroyed, and the Three Kings Islands will probably long remain a safe preserve of rare plants and rare birds.

Among the more distant islands of the New Zealand region recently explored botanically, the first to claim our attention is the Kermadec group. The group consists of four principal, widely separated islands; the largest, Sunday Island, being about twenty miles in circumference and nearly 650 miles distant from Auckland; or midway between New Zealand and Tongatabou. The centre is occupied by a crater more than a mile in diameter, the rim of which rises to 1720 feet in its highest part. Previous to the visit of our author, Mr. T. F. Cheeseman (5), almost nothing was known of the vegetation of this or any of the other islands of the group. Naturally, from the position of these islands, the composition of the flora was looked forward to with much interest. It has already been pointed out (*ante*, p. 31) how absolutely the New Zealand and Australian elements are wanting in the nearest parts of Polynesia. The results of the botanical investigation of Sunday and Macaulay Islands of the Kermadec group are instructive as showing how strongly the New Zealand element predominates, and how probable the hypothesis of a land connection between Eastern Australia and New Zealand, including intervening islands, though Cheeseman records it as his opinion that the Kermadecs were not included in this connection. Sunday Island, the only one thoroughly botanised by him, is clothed with forest from the sea-shore to the highest peaks; and, although, as we shall see, the affinities of the flora generally are much more strongly New Zealand than Polynesian, "the prevailing tree, forming two-thirds of the vegetation," is the common Polynesian *Metrosideros polymorpha*. This species does not occur either in Australia or in New Zealand or in Norfolk Island, but it is generally diffused in Polynesia, extending eastward to the Hawaiian, Marquesas and Pitcairn Islands. The Norfolk Island palm, *Rhopalostylis Baueri* (*Areca Baueri*), or a closely allied species, comes next in prominence and abun-

dance; and *Cyathea Milnei*, an endemic tree fern, is another conspicuous object, often attaining a height of fifty or sixty feet. From Mr. Cheeseman's tabulation of the distribution of the eighty-four phanerogams and thirty-one vascular cryptogams collected, we learn that eighty-five are also found in New Zealand, though only fourteen of them have no wider diffusion. Forty-seven extend to Polynesia, but of these no fewer than thirty-seven also inhabit New Zealand. About forty of the species also occur in Lord Howe's Island and in Norfolk Island, but with three or four exceptions they also occur in New Zealand; and the same may be said of those extending to Australia. Assuming the palm to be correctly identified, though Mr. Cheeseman does not appear to be absolutely certain on this point, it is the only one of the peculiar Norfolk Island plants found in the Kermadecs; and none of the peculiar Lord Howe Island plants occurs there. Finally it may be observed that the endemic element is exceedingly small considering the great isolation of the group; only six species being described as peculiar, namely, one herbaceous: *Scævola gracilis*, and five arboreous: *Coprosma acutifolia*, *Myrsine kermadecensis*, *Carumbium polyandrum*, *Bœhmeria dealbata* (at first confused with *B. australis*) and *Cyathea Milnei*.

Passing southward we encounter the Chatham Islands, concerning the botany of which there is nothing recent. Next come the Bounty Islands, in about 47° 30′ S. lat., which support no vascular plants (6), and then Antipodes Island, in about 49° 30′. Previous to 1890 the botany of this island was quite unknown, but during that year Mr. T. Kirk had an opportunity of landing there for a few hours (7). The island is the crater of an extinct volcano with a diameter of about two miles; the highest part being about 1300 feet. Its vegetation consists largely of coarse sedges and grasses, though plants with showy flowers are not altogether wanting; the beautiful *Pleurophyllum criniferum* (Compositæ) being as luxuriant as in the Auckland and Campbell Islands. *Stilbocarpa polaris* (Araliaceæ) is another prominent ornamental plant; and a new white-flowered gentian, *Gentiana antipoda*, was very abundant.

Senecio antipodus, a handsome herbaceous species, was the only other endemic plant collected. Woody plants were limited to three species of *Coprosma* (Rubiaceæ), two of which are prostrate shrubs, and the third, *C. cuneata*, rarely exceeds the stature of a low-growing bush. Including *Stellaria media* and *Poa aunna*, two naturalised plants, fifty-five species of vascular plants were collected, about forty of which are common to the main islands of New Zealand. A few are peculiar to Antipodes, Campbell and other "Antarctic" islands; among them: *Stellaria decipiens*, *Colobanthus muscoides*, *Ligusticum antipodum*, *Stilbocarpa polaris*, *Pleurophyllum criniferum* and *Chiloglottis cornuta*, a ground orchid. Mr. Kirk also visited Campbell Island (8) and the Auckland group (9) and succeeded in adding upwards of a dozen to the previously known plants from these islands. He found the handsome and striking herbaceous plants, for which these islands are famous, in their full glory. The genera *Ligusticum*, *Stilbocarpa*, *Pleurophyllum*, *Celmisia*, *Myosotis*, *Gentiana*, *Veronica* and *Bulbinella* are specially prominent in the vegetation. Unfortunately, cattle, sheep, goats and rabbits have been introduced into all these islands, and their unique flora is certain to suffer in consequence. The beautiful *Metrosideros lucida* is the principal tree in the Aucklands, but very rare in Campbell Island, where indeed no real arboreous vegetation exists. There are about twenty-five species of ferns in the Aucklands. But so much has been written on this subject that it will be sufficient to enumerate the plants not previously recorded. They are: *Ligusticum latifolium*, var. *angustatum*, *Pleurophyllum Gilliesianum*, *Lagenophora Forsteri*, *Samolus repens*, *Rumex neglectus*, *Phormium tenax*, *Juncus bufonius*, *Deschampsia gracillima*, *D. Hookeri*, *Lomaria dura*, *Aspidium cystostegia*, *Hymenophyllum villosum*, *H. polyanthos* and *H. bivalve*.

For the sake of completeness, reference may here be made to the flora of Macquarie Island, the most southernly of the outlying islands of the New Zealand region, though its exploration was previous to 1885 (10); and more especially as Mr. Kirk has published a revised list of the plants (11).

Mr. Scott's collection consisted of twenty-one species of vascular plants, all herbaceous, and including *Stilbocarpa* and *Pleurophyllum.* The majority of the others are such as are found all round in the coldest southern region of phanerogamic vegetation ; and there are no endemic species, which is quite in conformity with the conditions in other parts of the southern hemisphere, as well as in the northern coldest region of vegetation.

The botanical exploration of South Georgia by a German expedition (13) adds one more important link in the chain of "Antarctic" vegetation, and goes to strengthen the statement advanced by the writer (14), that the only admissible demarcation of the coldest southern floral region is a zonal one. That is to say, broadly speaking, the composition of the vegetation of the remotely separated exceedingly small islands in the southern seas, on the extreme limit of phanerogamic life, is practically the same all round the globe, and is in all probability the remains of a more extended and possibly continuous belt, because the present conditions cannot be accounted for by the ordinary means of dispersal. South Georgia is situated in about 54° S. lat. and 37° W. long.; thus being 20° east of the Falkland Islands and in a somewhat higher latitude. It was discovered by Captain Cook in January, 1775; and at least one of the Forsters, the botanists of the expedition, was among the party that landed, but they found very little vegetation. Cook describes the island as of the most desolate and barren nature conceivable, observing that the only vegetation met with was a coarse grass, a kind of burnet, and a moss-like plant growing on the rocks. Foster does not even mention these plants in his reference to the island. The members of the German expedition spent nearly a year on the island, and Dr. Will collected thirteen species of phanerogams, namely: *Ranunculus biternatus, Colobanthus subulatus, C. crassifolius, Montia fontana, Acæna adscendeus, A. lævigata, Callitriche verna, Juncus Novæ-Zealandiæ, Rostkovia magellanica, Aira antarctica, Phleum alpinum, Festuca erecta* and *Poa flabellata.* Some of the plants were found in abundance

and flourishing luxuriantly. Three of the species have a wide range, and belong to the British flora; but the remainder are peculiar to the cold regions of the southern hemisphere. No less than nine out of the thirteen occur in some of the outlying islands of the New Zealand seas.

We may now pass to what may conveniently be termed the American Pacific Islands.

Ever since the publication of Sereno Watson's account of a botanical collection made by Dr. E. Palmer in Guadeloupe Island, Lower California (15), American botanists have lost no opportunity of continuing the exploration of what may be termed the Californian Archipelago. The same botanist has again visited Guadeloupe Island and brought away large collections. This island is situated about 100 miles from the mainland, is twenty-six miles long, with an average breadth of ten miles, and has a central mountain ridge rising to nearly 4000 feet above the level of the sea. In the article alluded to the composition of the flora is carefully analysed, and found, like that of Lower California generally, to be an extension of the Californian flora rather than the Mexican of the same latitude. Trees are plentiful over much of the island, and often of considerable dimensions. Prominent among them are, an oak (*Quercus tomentella*), a pine (*Pinus insignis*, var. *binata*), a juniper (*Juniperus californica*), and a cypress (*Cupressus macrocarpa*). Besides these there is an endemic palm (*Erythea edulis*), "the only thing on the island having a tropical look". It has fan-shaped leaves, grows thirty to forty feet high, and bears clusters of fruit forty to fifty pounds in weight, which is eaten "by man, goats, birds and mice". The discovery of an endemic palm with an edible fruit has, of course, not been paralleled in subsequent explorations; but a number of less prominent plants are new (16). One hundred and forty-five species have been collected in the island, and of these thirty have not been found elsewhere. These are nearly all herbaceous plants, belonging to natural orders characteristic of the region. In order to complete the botanical bibliography reference should be made to the visit of another botanist (17), who among other

novelties discovered the only two members of the Cactaceæ (*Mamillaria Goodrichii* and *Opuntia prolifera*) known to inhabit the island. Many interesting observations are embodied in Mr. Greene's notes. One notable fact is the presence of thousands of goats without "any perceptible injurious effect on the vegetation". Indeed, a small body of Mexican soldiers was kept on the island to prevent freebooters from continuing the destruction of the goats, as ship-loads of goat-skins and tallow had previously been exported in this way to San Diego. The disastrous effects of the introduction of goats where there was scarcely any herbaceous vegetation, as in St. Helena, is too well known; they ate the young seedlings and browsed on the shrubby vegetation to an extent that soon made it impossible for reproduction or propagation of any kind to proceed. It is probable, however, that the goats are preventing the developement of young plants in the island of Guadeloupe; for Greene, who was ten years later than Palmer's first visit, specially notes the rapid disappearance of the old trees without any corresponding increase of young ones. It will be sufficient to give references (18) to some of the more important of the numerous lists of plants collected in the Californian Islands. Some of them, however, are much more than lists, and contain facts of great value in phytogeography. Thus Brandegee tabulates the 512 species of vascular plants found in the five islands named. Only twenty-six of this number had not at that date (1890) been found on the mainland, and it was assumed that further explorations would considerably reduce this apparently endemic element. One peculiarity of the flora of this group of islands is that it is more southern in character than the immediately opposite part of the mainland, between 33° and 34° N. lat. Cedros Island, just outside of the Bay of San Sebastian Viscaino, in about 28° lat., and about forty miles from the mainland, though of extremely barren appearance, has a very curious though meagre flora. It is very rugged, of volcanic origin, with peaks rising to an altitude of 4000 feet; somewhat triangular in outline, and a little over twenty miles in its greatest diameter. An exploring party visited the island

as long ago as 1859; and Dr. Veatch, one of the party, brought away dried specimens of a few plants, including a very singular one described below; but he, who was not a botanist, reported the island as nearly destitute of vegetation. Since then several botanists have visited Cedros; and the latest summary gives the number of phanerogams recorded as 135 species. With regard to the name Cedros, it should be explained that there are neither cedars nor cypresses in the island, and it seems probable that the name Cerros of the older maps and gazetteers is the correct one; but Greene (19) argues that the contrary is the case and that the island received its name from the presence of a juniper (*Juniperus cedrosianus*), although this juniper is neither plentiful nor prominent, being at the most ten to fifteen feet high, and often a dwarf shrub. Open groves of a pine (*Pinus muricata*) exist on the higher slopes, some of the trees being probably as much as seventy feet high. The Dr. Veatch mentioned above collected most of the specially peculiar plants of the island, and although they were described and a number of them figured as long ago as 1862, it may be desirable to give a reference to the place (20), because it is a publication found in few libraries in Europe. Remarkable among the trees is the anacardiaceous *Veatchia cedrosensis* (*Rhus Veatchiana*). Greene writes: "The most conspicuous objects everywhere were the clumps of what Dr. Veatch and his party so naturally denominated the elephant tree. These trees at our time had not put forth their leaves, and their low, thick, unwieldy trunks, of which there were always several from the same root, clothed with a perfectly smooth, gray, skinny bark which looks like the distended skin on a very fat animal, could hardly fail to suggest the limbs of the elephant. There are no parts of the island, except the higher elevations, upon which this tree does not thrive; but the largest specimens were seen in the arroyos, not far back from the shore. Agreeably to its aspect of a swollen limb, the epidermis of the trunk is really, as it were, distended by a very thick, soft, inner bark, more than an inch in depth, which, when cut, exudes a great quantity of some

gummy or pitchy substance." Greene gives particulars of the height of this tree; but Palmer describes it as "a dwarf tree five to six feet high". Brandegee has identified it (21) with *Schinus discolor* (22) found in Magdalena Bay, Lower California; but we think erroneously, though we have not space to discuss the question here. *Hauya arborea* (*Œnothera arborea*) is another remarkable plant from Cedros Island. It can hardly belong to either of the genera to which it has been referred; certainly not to the latter. Indeed, we think there is very little doubt about its being a species of *Zauschneria*, and perhaps only a shrubby condition of *Z. californica*, which is known to vary very much under different conditions. The name *arborea* is a little misleading, because, although the plant becomes woody, it only grows six to eight feet high, and seldom exceeds two or three inches in diameter. The anomalous Mexican and Lower Californian genus *Fouquieria*, which has been referred to such widely different orders as the Polemoniaceæ and Tamariscineæ, is represented by a yellow-flowered species of singular habit, named *F. columnaris*, but originally a new genus under the name of *Idria*. *Agave Sebastiana* is an endemic species, well represented in a view of one of the bays of the island in the earliest publication cited (20). Greene's report (19) contains many more highly interesting details; but until the botany of the mainland of Lower California is better known it would be idle to speculate whether the numerous strange plants found in Cedros Island are really endemic.

Proceeding southward we come to the Revillagigedo Islands, the largest of the group, lying nearly in the same longitude as Cape San Lucas, Lower California. These islands have never been thoroughly botanised; yet, as they are upwards of 250 miles from the nearest part of the mainland, or any land, with an elevation of 2000 feet, some interesting results might be expected. Mr. C. H. Townsend, the ornithologist of the *Albatross* expedition, referred to below, collected a few plants in Socorro, the largest island of the group, twenty-four miles long by nine miles broad, and in Clarion or Cloud Island, about 4° to the west-

ward. The few collected are published (23) and the authors state that the flora is doubtless tropical and similar to that of Mexico. Judging from the list of plants, it would be more correct to designate the flora as subtropical, although the islands are within the tropics. The total number of species found on the two islands was twenty-six; eighteen in Socorro and twelve in Clarion, four being common to the two. *Teucrium Townsendii* and *Cardiospermum Palmeri* are described as new; but the latter had previously been collected in Lower California. Most of the other plants are common, or at least belong to common genera; but as ten of them have not been determined some doubt remains on this point. It is clear, however, that the indigenous flora has hardly been tapped.

The Galapagos are the next group claiming our attention.

In 1884 the Italian corvette *Vettor Pisani*, on a voyage round the world, put in at the Galapagos, where ten days were spent; and Lieutenant Chierchia made a small collection of plants on Chatham and Floriana, or Charles, Islands. This was worked out and published by Professor Caruel (24). It is little more than a bare list and adds nothing important to previous knowledge of the flora, though two species are described as new, namely: *Polygonum galapagense* and *Cyperus galapagensis*. There is a specimen of the former at Kew, and it is probably an endemic plant; but it requires a very special knowledge of *Cyperus* to give an opinion as to the validity of the proposed new species. The Americans lost a good opportunity of increasing our knowledge of the flora of the Galapagos and of Cocos Island to the north-east, in connection with the voyage of the *Albatross;* for although a few plants were collected (25) next to nothing was added to what was previously known. In Professor Agassiz's general sketch of the work of the expedition (26) there are many interesting details on the aspects and composition of the three belts of vegetation in the Galapagos first described by Wolf (27) "which can be recognised on all the islands". The illustrations afford an excellent idea of the physiognomies of these belts of vegetation. Particularly striking in the lower or more barren belt

are the huge branching Cacti. Unfortunately the author's knowledge of botany was insufficient to enable him to describe adequately what he saw. There are excellent maps accompanying this report. Concerning the origin of the fauna and flora of the Galapagos, Agassiz vigorously attacks and ridicules Baur's theory of subsidence, put forward with so much confidence (28), and briefly stated thus: "My conclusion, therefore, is, the Galapagos are continental islands originated through subsidence. They all formed at a past period one large island, and this island itself was at a still former period in connection with the American continent." It will be sufficient to have directed attention to the discussion here. It is worth adding, however, that Baur's article is supplemented by an excellent bibliography.

In the same publication Cocos and Malpelo Islands are also represented by photographs and present a striking contrast to each other. The one is a cone, covered with vegetation from the sea to the summit; the other a barren rocky mass with steep, almost perpendicular, cliffs, recalling the Island of St. Helena. It is a pity that arrangements were not made to investigate thoroughly the fauna and flora of Cocos Island; for although it was visited by many of the early voyagers, such as Dampier, Vancouver, Anson and Wafer, who each described it more or less fully, it has rarely been touched by later expeditions, and by none, I believe, for scientific purposes, since the visit of H.M.S. *Sulphur*, upwards of fifty years ago. From all accounts, its vegetation is totally different from that of the Galapagos, being quite tropical in character and including a variety of trees of large size, and tree-ferns as much as twenty feet high. The *Sulphur* expedition brought home specimens of about a dozen flowering plants, two-thirds of which were described as new and peculiar to the island. The few plants collected by Agassiz here and in the Galapagos are enumerated (25), but they contain nothing of interest. One, *Oxalis Agassizi*, from the Galapagos, is described as new.

Leaving the Galapagos for the distant southern Juan Fernandez, or John Fernando, as some of the earlier English navigators translated it, I have one most impor-

tant discovery to chronicle. It has been on record for nearly fifty years (29) that a kind of sandal-wood was, in earlier times, very common in the island; and also that it all perished (from what cause we are not told, but the assumption is from an unusually low temperature) in one and the same year. This bare statement was in a manner supported by the undoubted existence of dead trunks having the anatomical characters of sandal-wood. Otherwise the probabilities were against the correctness of this record, because there is no true *Santalum* in America, and the nearest habitat of any species of the genus is in the Marquesas Islands, some 3500 miles to the north-west of Juan Fernandez. But unimpeachable evidence, in the form of living specimens in flower, has come to light; and Mr. F. Philippi (30) has figured and described the species under the name of *Santalum fernandezianum*. Judging from the figure and an imperfect specimen lately sent to Kew by the author, it is near, though distinct from, *S. Freycinetianum*, which inhabits the Marquesas, Society and Hawaiian Islands, and very different from the Indian *S. album*, to which Gay referred it in the work cited above. A recent work (31) on the ferns of Juan Fernandez merits attention for the very careful manner in which the author has worked out the geographical and biological details from observations on the spot. The number of species enumerated is forty-five, being one more than enumerated by the writer (32); and seven of them are endemic. It is a singular and unaccountable fact that the Lycopodiaceæ are not represented in these islands.

BIBLIOGRAPHY.

(1) HOOKER. Icones Plantarum, t. 2250. *Transactions of the New Zealand Institute*, xxv., p. 269, t. 20.

(2) T. KIRK. On the Flowering Plants of Stewart Island. *Transactions of the New Zealand Institute*, xvii., pp. 213-228, 1885. On the Ferns and Fern Allies of Stewart Island. In *op. cit.*, pp. 228-234. See also D. Petrie, vol. xiii., pp. 323-332, for complete list of plants then known.

(3) T. KIRK. On the Botany of the Snares. *Transactions of the New Zealand Institute*, xxiii., pp. 426-431, 1891. Also *Journal of Botany*, pp. 206-208, and 236-239, 1891.

(4) T. F. CHEESEMAN. Notes on the Botany of the Three Kings Islands. *Transactions of the New Zealand Institute*, xx., pp. 141-150, 1888.

T. F. CHEESEMAN. Further Notes on the Three Kings Islands. *Transactions of the New Zealand Institute*, xxiii., pp. 408-424, 1891.

(5) T. F. CHEESEMAN. On the Flora of the Kermadec Islands. *Transactions of the New Zealand Institute*, xx., pp. 151-181, 1888.

(6) See reference, n. 12.

(7) See reference, n. 12.

(8) See reference, n. 12.

(9) T. KIRK. Report on a Botanical Visit to Lord Auckland and other Antarctic Islands. *Journal of the Linnæan Society*, xxviii., pp. 327-330, 1891.

(10) J. H. SCOTT. On the Fauna and Flora of Macquarie Island. *Transactions and Proceedings of the New Zealand Institute*, xv., pp. 484-493.

(11) T. KIRK. On the Flora of Macquarie Island. *Report of the Third Meeting of the Australasian Association for the Advancement of Science*, pp. 226-227, 1891.

(12) T. KIRK. On the Botany of the Antarctic Islands, generally of the New Zealand region. *Report of the Third Meeting of the Australasian Association for the Advancement of Science*, 1891. The Snares, p. 214; The Auckland Islands, p. 218; Campbell Island, p. 222; Macquarie Island, p. 226; Antipodes Island, p. 228; and the Bounty Islands, p. 231.

(13) Dr. WILL. Die Phanerogamenflora von Süd-Georgien. Nach den Sammlungen, bearbeitet von A. Engler. *Botanische Jahrbücher*, vii., pp. 281-285. Vegetation of South Georgia. W. Botting Hemsley. *Nature*, xxxiv., pp. 106-107, 1886. A reproduction of Engler's main facts, with some historical notes and remarks.

(14) *Report on the Scientific Results of the Voyage of H.M.S. "Challenger". Botany*, i., Introduction, p. 51.

(15) S. WATSON. On the Flora of Guadeloupe Island, Lower California. *Proceedings of the American Academy of Arts and Sciences*, xi., pp. 105-121, 1876.

(16) G. VASEY and J. N. ROSE. List of Plants collected by Dr. Edward Palmer, in Cedros, San Benito and Guadeloupe Islands. *Contributions from the U.S. Herbarium*, i., pp. 13-27, 1890.

(17) E. L. GREENE. Notes on Guadeloupe Island, with a Catalogue of the Plants. *Bulletin of the Californian Academy*, i., pp. 214-228.

(18) T. S. BRANDEGEE. Flora of the Californian Islands, San Clemente, Santa Catalina, Santa Cruz, Santa Rosa and San Miguel. *Zoe*, i., pp. 129-148, 1890.

(19) E. L. GREENE. Flora of San Miguel, Cedros and San Benito Islands. *Pittonia*, i., pp. 74-93, 194-208, and 261-269, 1887-1889.

(20) A. KELLOGG. Descriptions and Figures of New Plants from Cedros Island and elsewhere. *Proceedings of the Californian Academy of Natural Sciences*, ii., 1859, *passim*. The coloured plates first appeared in *The Hesperian*, and for the third time, with corrections, in the nomenclature, by Mary E. Curran, in the *Bulletin of the Californian Academy of Sciences*, i., No. 2, pp. 128-151, 1885.

(21) *Proceedings of the Californian Academy of Sciences*, 2nd series, ii., p. 140.

(22) G. BENTHAM. *Botany of the Voyage of the "Sulphur,"* p. 11, pl. 9.

(23) G. VASEY and J. N. ROSE. Plants collected at Socorro and Clarion Islands. *Proceedings of the U.S. National Museum*, xiii., pp. 145-149, 1890.

(24) T. CARUEL. Contribuzione alla Flora delle Galapagos. *Rendiconti della R. Accademia dei Lincei*, v., pp. 619-625, 1889.

(25) J. N. ROSE. List of Plants collected by the U.S. S. *Albatross* along the western coast of America, Cocos Island and Galapagos Islands. *Contributions from the U.S. National Herbarium*, i., pp. 135-138, 1892.

(26) ALEXANDER AGASSIZ. General Sketch of the Expedition of the *Albatross*. *Bulletin of the Museum of Comparative Zoology at Harvard College*, xxiii., 1892; plates.

(27) Ein Besuch der Galapagos Inseln, mit drei Kärtchen. Heidelberg, 1870.

(28) G. BAUR. On the Origin of the Galapagos Islands. *The American Naturalist*, xxv., pp. 217-229, and 307-326, 1891.

(29) CLAUDIO GAY. Historia Fisica y Politica de Chile. *Botanica*, v., p. 326.

(30) F. PHILIPPI. Der Sandelholzbaum von Juan Fernandez. *Botanische Abhandlungen*, Leipzig, 1893. *Aus den Anales del Museo Nacional de Chile*.

(31) F. JOHOW. Los Helechos de Juan Fernandez. *Los Anales de la Universidad de Chile*, 1893. Also issued separately.

(32) *Report on the Scientific Results of the Voyage of H.M.S. "Challenger". Botany*, vol. i., part iii.

W. BOTTING HEMSLEY.

THE NEW THEORY OF SOLUTIONS.

(*Continued from p.* 26.)

THE well-known equation PV = RT which expresses in the case of a gas both the laws of Boyle and Guy Lussac may be made to include Avogadro's hypothesis. As Horstmann first pointed out, if we decide that in all cases our unit of weight shall be a number of grams numerically equal to the molecular weight of the particular gas with which we are dealing, the constant R will then have the same value for all gases which conform to Avogadro's hypothesis, for under the same conditions of temperature and pressure the volume occupied by unit weight will be the same for all. If the pressure P be measured in atmospheres and the volume V in litres, and if T be the absolute temperature, the volume energy of a gram-molecular weight of an ideal gas is given by—

$$PV = \cdot 0819\ T.$$

The direct observations on osmotic pressure indicate that precisely the same expression holds for a dilute aqueous solution of an indifferent substance if P be now the osmotic pressure, and V the volume of the solution which contains a gram-molecular weight of dissolved substance.[1]

On account of the difficulties besetting the experimental methods and from the fact that aqueous solutions alone have at present been investigated, the support lent by direct observations on osmotic pressure to the validity of the above expression in the case of solutions is not very extensive.

[1] Pfeffer's results expressing the relation between the osmotic pressure P′ measured in cm. of mercury, the ordinary temperature t, and C the number of grams of sugar in 100 gr. of water may be summarised by—

$$P' = 49{\cdot}27\ C\ (1 + {\cdot}00367t).$$

On assuming the densities of the dilute solutions employed to be the same as that of water and on calculating from this equation the pressure P in atmospheres for V litres of solution containing a gram-molecular weight, *i.e.*, 342 gr. of sugar at the absolute temperature T, we obtain—

$$P = 49{\cdot}27 \times 342\ T/760\ V \times 273,$$

which is PV = ·0812 T.

Fortunately, however, several important indirect methods may be employed in dealing with this question. The magnitude of the osmotic pressure may be connected with those of other properties of solutions, properties which can be readily measured for solutions in different solvents and which may thus be employed to test the general validity of the equation PV = ·0819 T. Indeed, in the process of accumulating this indirect testimony the new theory of solutions has rendered one of its most important services. For here it has been emphasised that the properties involved are correlated properties, and although this correlation is in no way dependent upon any assumption as to the nature of osmotic pressure or the state of dissolved substances, the application of the conception of osmotic pressure must be credited with giving for the first time due prominence to this interdependence, the recognition of which goes far to generalise the laws of dilute solutions.

The property which in the first instance may be conveniently investigated, as giving indirect support to the application of gaseous laws to dilute solutions, is vapour-pressure.

VAPOUR-PRESSURE.

It can be readily shown theoretically that the partial pressure of the vapour of a solvent over a solution must be less than the vapour-pressure of the pure solvent at the same temperature. Consequently, if the dissolved substance be non-volatile, the vapour-pressure of the solution will be less than that of the pure solvent. This conclusion is in harmony with the well-known facts that at the same temperature the vapour-pressure of a solvent is lowered, and under the same external pressure the boiling-point of a solvent is raised, by the presence of a non-volatile dissolved substance.

Experimental results.—The investigation of the vapour-pressures of indifferent solutions has been carried out almost entirely by F. M. Raoult, who in 1886 began to communicate observations on the subject. His original measurements were made by means of Dalton's statical method, but eventually a dynamical or boiling-point

method was also employed in estimating the vapour-pressures. If, at any temperature, p be the vapour-pressure of the solvent, and p' be the vapour-pressure of the solution of a *non-volatile* dissolved substance, the ratio $(p - p')/p$, which is now commonly termed the *relative lowering* of the vapour-pressure, was found to obey the following laws :—

Influence of temperature.—Within the limits of the experimental errors Raoult's results were in agreement with *von Babo's law.* This law, deduced as early as 1847 from observations on aqueous saline solutions, implies that the relative lowering of the vapour-pressure is the same at all temperatures. In testing this conclusion measurements were made upon solutions in ether, benzene, alcohol, and acetic acid, over temperature ranges varying between 20° and 40°.

Influence of concentration.—In his first communication, which dealt with solutions containing from one to five gram-molecules of substance dissolved in 5000 gr. of ether, Raoult found that the relative lowering was almost proportional to the weight of substance dissolved in a constant weight of ether. Hence, expressing the concentration in gram-molecular weights, if n gram-molecules of substance be dissolved in N gram-molecules of solvent, we have that—

$$(p - p')/p = \mathrm{K}\, n/\mathrm{N},$$

where K is a constant. *Wüllner's law* (1856-60), derived from measurements of the vapour-pressures of aqueous solutions of simple and mixed salts, and which implies that the relative lowering is proportional to the concentration, embodied the same conclusion.

Trustworthy experiments on more dilute solutions are difficult to make on account of the large value of the experimental error, and in subsequent papers Raoult has, in general, dealt with solutions which are more concentrated than those usually employed in ascertaining the laws of ideal solutions. From measurements on ethereal solutions containing 17 to 70 gram-molecules of substance in 100 of solution he was led to express the effect of concentration by—

$$(p - p')/p = \mathrm{K}'n/(\mathrm{N} + n)\,;$$

the relative lowering being proportional not to the number

of molecules of substance in a constant number of molecules of solvent (as Wüllner's law requires), but in a constant number of molecules of *solution*. The value of K′ was found to vary with the nature of the solution; in the case of six solutions in ether, benzene, and alcohol, the extreme values were ·73 and ·97.

For more dilute solutions containing from 3 to 15 gram-molecules per 100 of solution K′ in all cases approximated to the value 1, so that here the general law appeared to be—

$$(p - p')/p = n/(N + n).$$

For the most dilute of the above solutions and for still more dilute solutions $n/(N + n)$ is practically the same as n/N. Raoult's observations may therefore be taken to indicate that for the most dilute solutions $(p - p')/p = n/N$, or that Wüllner's law is approximately obeyed.

Measurements of the boiling-points of solutions (*vide infra*), where smaller concentrations may be used, lead to a similar conclusion, which, on employing the ordinary method of denoting the concentration, may be expressed by stating that if g grams of substance be dissolved in 100 gr. of solvent then $(p - p')/pg$ is approximately constant; in general, as g increases the value of this quantity slowly diminishes, although in some cases its value slowly increases.

Influence of the chemical nature of the dissolved substance.—The most interesting result arrived at by Raoult was that dilute solutions in the same solvent, having the same molecular concentration, have the same vapour-pressure. His numbers showed that if M′ be the molecular weight of the dissolved substance, $M'(p - p')/pg = C$ was a constant. This quantity he termed the *molecular lowering* of the vapour-pressure; it is evidently the lowering which would be produced by the dissolution of a gram-molecular weight of substance in 100 gr. of solvent if Wüllner's law were valid for such a strong solution. That Wüllner's observations on aqueous saline solutions gave some indication that the molecular depression was approximately constant had previously been pointed out by Ostwald in 1884. The following table contains the data given by Raoult to demonstrate the constancy of the molecular lowering in the case of ethereal

solutions. The concentrations of the solutions employed varied between 1 and 5 gram-molecules of substance per 5000 gr. of ether.

Dissolved Substance.	M′.	C.
Cyanamide	42	·74
Cyanic Acid	43	·70
Aniline	93	·71
Benzaldehyde	106	·72
Benzoic Acid	122	·71
Capryl Alcohol	130	·73
Turpentine	136	·71
Methyl Salicylate	152	·71
Trichloracetic Acid	163·5	·71
Antimony Trichloride	228·5	·67
Hexachlorethane	237	·71
Mercury-ethyl	258	·69
Methyl Azocuminate	382	·68

The average value of C is ·71 and the mean divergence is only ·01, although the dissolved substances belong to families of widely different chemical character and have molecular weights, which in the extreme cases are in the ratio of 1 to 9.

Influence of the chemical nature of the solvent.—Raoult further found empirically that if M be the molecular weight of the solvent, C, the molecular lowering, is practically equal to M/100. The mean values of C obtained from observations on different substances dissolved in twelve different solvents are compared in the following table with the corresponding values of M/100.

Solvent.	C.	M/100.	100 C/M = A.
Water	·185	·18	1·02
Methyl Alcohol	·33	·32	1·03
Acetone	·59	·58	1·01
Amylene	·74	·70	1·06
Ether	·71	·74	·96
Carbon Bisulphide	·80	·76	1·05
Benzene	·83	·78	1·06
Ethyl Bromide	1·18	1·09	1·09
Chloroform	1·30	1·20	1·09
Phosphorus Trichloride	1·49	1·38	1·08
Methyl Iodide	1·49	1·42	1·05
Carbon Tetrachloride	1·62	1·54	1·05

In the last column are given the values of 100 C/M, which, if Raoult's conclusion be valid, should be unity. The mean value is 1·03, the average divergence being ·03. The whole of the foregoing empirical results may therefore be expressed by—

$$\{(p - p')/pg\} \times (100\ M'/M) = A \qquad (1)$$

where A is very nearly equal to unity and is evidently the diminution of the vapour-pressure produced on dissolving 1 gram-molecule of substance in 100 gram-molecules of solvent. Since Wüllner's law is not strictly obeyed, the values of A, which were obtained for solutions containing 4 to 12 gram-molecules of substance per 100 of solution, depend to some extent on the concentrations of the particular solutions employed. For more dilute solutions, however, the values will be practically the same.[1]

That the value of A should not be exactly unity but might in particular cases be considerably larger, became evident from a study of solutions in acetic acid, made by Raoult and Recoura in 1890. For these solutions A had the exceptional value of 1·63. Now acetic acid differs from all the solvents in the preceding table in having an abnormal vapour-density, and at the temperature at which the vapour-pressure observations were made, d'/d, the ratio of the actual to the theoretical vapour-density is 1·64 and thus almost identical with the value of A. It was therefore concluded that $A = d'/d$, and a reason was thus furnished for the mean value of A already given being slightly greater than unity, because, in general, the densities of the saturated vapours of the solvents used are slightly larger than the theoretical values. The following table (Raoult, 1893) gives for six solvents, at the temperature t, the values of A as obtained from the vapour-pressures of dilute solu-

[1] If A be deduced from the depression produced by 1 gram-molecule of substance per 100 of *solution* its mean value A′ is slightly lower than 1·03, *viz.*, ·98. If, however, values of A′ be determined in the case of each dissolved substance for concentrations varying between 3 and 15 gram-molecules per 100 of solution, and the values of A′ be then found for an extremely dilute solution by treating A′ as a function of the concentration, the numbers thus obtained for A′ are almost the same as those above obtained for A.

tions, and those of d'/d as derived from direct observations of vapour-density.

Solvent.	t.	A.	d'/d.
Water	100	1·02	1·03
Ethyl Alcohol . .	78	1·01	1·02
Ether	20	1·04	1·04
Carbon Bisulphide . .	24	·99	1·01
Benzene . . .	80	1·01	1·02
Acetic Acid . . .	118	1·63	1·64

The accord between the two series of numbers leaves little doubt that $A = d'/d$.

General conclusions.—The whole of Raoult's results may therefore be represented by—

$$\{(p - p')/pg\} \times (100\ M'/M) = d'/d \qquad (2).$$

If n be the number of gram-molecules of substance dissolved in N gram-molecules of solvent, $n = g/M'$ and $N = 100/M\ (d'/d)$ where $M \times d'/d$ is the average molecular weight of the solvent as calculated from its vapour-density at the temperature of the experiment. We may therefore write (2) as—

$$(p - p')/p = n/N \qquad (3)$$

and arrive at the remarkably simple empirical result that *the relative lowering of the vapour-pressure is equal to the ratio of the number of gram-molecules of dissolved substance to the number of gram-molecules of solvent present in the solution.* It is well to note that (3) can only hold for dilute solutions as it leads to the erroneous conclusion that when the solution is so strong that $n = N$, the vapour-pressure of the solution is *nil.* For concentrated solutions, as has already been stated, the equation—

$$(p - p')/p = n/(N + n)$$

has to be employed to express the facts.

Vapour-pressure and the gaseous laws.—If two solutions in the same solvent have at the same temperature the same osmotic pressure they must have the same vapour-pressure.

Let two solutions A and B (fig. 1) be introduced into a hollow ring-shaped vessel and let them be separated by a semi-permeable membrane MM. If the solutions are isotonic, at the outset there will be no change in their concentrations due to passage of solvent through MM. If, however, the vapour-pressure of A be supposed greater than that of B, solvent will pass from A to B by evaporation, and to restore the osmotic equilibrium solvent will have to pass from B to A through MM. A continuous isothermal circulation of solvent would thus proceed automatically at the expense of the heat of surrounding objects and a result would thus be obtained which is opposed to the second law of thermodynamics. In this way it may be shown that the vapour-pressures of isotonic solutions must be equal.

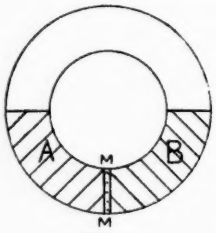


FIG. 1.

Now Raoult's empirical results have proved that solutions having the same vapour-pressure have the same molecular concentration. These results furnish, therefore, another means of showing that Avogadro's hypothesis is applicable to solutions, that, in fact, solutions of the same molecular concentration have the same osmotic pressure.

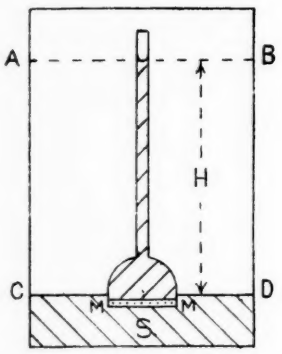


FIG. 2.

Indeed, the following simple discussion, based upon considerations due mainly to Arrhenius, serves to prove that Raoult's results taken collectively constitute an indirect demonstration of the general validity of the equation $PV = 0819\ T$ as applied to dilute solutions.

Let a quantity of solvent S be placed in an evacuated enclosure ABCD (fig. 2) kept at constant temperature T, and let an upright vessel, the base of which is a semi-permeable partition MM, dip into the sol-

vent, and let the vessel contain a quantity of a solution of a non-volatile indifferent substance. When equilibrium is established between solvent and solution the level of the latter AB will be at a definite height H above CD the level of the solvent, and if ρ be the density of the solution its osmotic pressure P will be $H\rho$. Now, in order that this condition of equilibrium may remain undisturbed, the solution must neither gain nor lose liquid by evaporation, that is, the vapour-pressure of the solution at the level AB must be equal to the pressure exerted by the vapour of the solvent at the same level. If this were not the case it could be shown in the manner already indicated that a continuous isothermal circulation of solvent would ensue. But if p be the vapour-pressure of the pure solvent or the pressure of the vapour at the level AB, the pressure p' at the level CD and thus the pressure of the solution will be less than p by the pressure exerted by a head of vapour equal to H. Consequently if d be the density of the vapour, $p - p' = Hd$, and since $P = H\rho$ we have—

$$P/(p - p') = \rho/d. \qquad (4).$$

We may now express d in terms of M the molecular weight of the solvent. The mean pressure of the vapour lies, of course, between p and p'; since, however, the solutions are dilute and p and p' differ but slightly, we may take p to be the pressure of the vapour. If further the vapour be assumed to behave as a perfect gas, $pv = \cdot0819\ T$ where v is the volume in litres occupied by M gr. of vapour. Thus $d = M/v = Mp/\cdot0819\ T$ and therefore—

$$P = (\cdot0819\ \rho T/M) \times \{(p - p')/p\}.$$

Now Raoult has shown that $(p - p')/p = n/N$, hence—

$$P = \cdot0819\ n\rho T/NM \qquad (5).$$

Here NM is the weight in grams of the amount of solvent which contains n gram-molecules of dissolved substance. If we neglect the weight of the dissolved substance and if we assume that the density of the solvent is the same as that of the solution,[1] the volume V of solution which con-

[1] Since the litre is employed as the unit of volume, ρ will not be the ordinary density of the solution, *i.e.*, the weight of 1 c.c., but the weight of 1 litre.

tains one gram-molecule of dissolved substance is $NM/n\rho$. On introducing V into (5) we obtain—

$$PV = \cdot 0819\ T.$$

Raoult's results, therefore, lead to the conclusion that in dilute solution dissolved substances obey gaseous laws. Equations (4) and (5) make it possible to calculate the values of the osmotic pressure from vapour-pressure observations, and the entire discussion makes it evident that vapour-pressure observations support the idea which has not yet been confirmed by direct experiment that osmotic pressure is independent of the nature of the solvent.

Equation (5) can only apply to very dilute solutions, as it involves the assumption that p and p' differ by so little that the density of the vapour may be taken to correspond with the pressure p. If we avoid this assumption by taking note of the actual fall of pressure on passing from CD to AB, the vapour being assumed to obey gaseous laws, we obtain—

$$P = (\cdot 0819\ \rho T/M) \times (\log_e p/p') \qquad (6).$$

It is interesting to note that if we substitute for P the corresponding gaseous pressure this equation may be reduced, as Ostwald has shown, to—

$$(p - p')/p = n/(N + n),$$

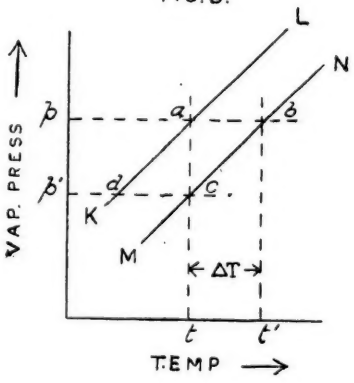
or the expression derived empirically by Raoult for strong solutions and which is therefore in harmony with theoretical considerations.

As has been mentioned the relationship between vapour-pressure and osmotic pressure was first established by van't Hoff in 1886. His mode of treatment consists essentially in equating the amount of work required to remove a definite amount of solvent from a solution by causing it to pass through a semi-permeable wall to amount required to remove the same quantity by evaporation at the same temperature. By this method van't Hoff and Gouy and Chaperon (1888) have arrived at relationships which are essentially the same as those given above.

BOILING-POINT.

If KL be a portion of the vapour-pressure curve of a solvent, and MN be a portion of the curve for solution of a non-volatile substance, at the temperature t, ac is equal to $p - p'$, the diminution in the vapour-pressure of the solvent brought about by the presence of the dissolved substance; and at the pressure p, ab is equal to $t' - t$ or ΔT, the corresponding rise in the boiling-point of the solvent. If ΔT be obtained experimentally the measurements may be utilised in two ways. If the vapour-pressure curve of the solvent be known we may read off the change $p - p'$ in the vapour-pressure p, which corresponds with the temperature difference ΔT, and the value of $(p - p')/p$ may then be used in the vapour-pressure formulæ already considered. On the other hand, the following treatment due to Arrhenius (1889) shows how the values of ΔT itself may be employed as a convenient means of investigating the vapour-pressure laws of dilute solutions.

FIG. 3.



If ΔT be small, that is, if the solution be dilute, the two curves KL and MN (fig. 3) may be taken to be straight and parallel, hence we may assume that $p - p' = \Delta T \tan adc = \Delta T\ dp/dt$ where dp/dt is the rate of change of the vapour-pressure of the solvent at its boiling-point, t, and thus a constant. On introducing the above value of $p - p'$ into Raoult's empirical vapour-pressure equation (1) we obtain—

$$M'\Delta T/g = A p M/100(dp/dt) \qquad (7).$$

From the ordinary thermodynamical relationship expressing the heat of vaporisation of a liquid in terms of the volume, pressure, and temperature of the vapour to which it gives rise, on neglecting the volume of the liquid which is small

as compared with that of the vapour, and on assuming the vapour to obey gaseous laws, it follows that—

$$dp/dt = M\lambda p/2T^2 \qquad (8)$$

where λ is the heat of vaporisation in calories of 1 gram of solvent at T, its boiling-point on the absolute scale. Substituting for dp/dt in (7) on putting A = 1 we obtain—

$$M'\,\Delta T/g = \cdot 02T^2/\lambda \qquad (9).$$

$M'\Delta T/g$ is the *molecular rise* in the boiling-point, or the rise which would be produced on dissolving a gram-molecule of substance in 100 gr. of solvent if ΔT remained proportional to g, *i.e.*, to the concentration. The equation indicates that the molecular rise should be the same for all dissolved substances and should depend solely upon the physical constants of the solvent.

The following examples taken from the extensive observations of Beckmann serve to illustrate the degree of approximation with which these deductions correspond with the results of experiment.

SOLUTIONS IN BENZENE.

Anthracene M′ = 178.			Benzoic Anhydride M′ = 226.		
g.	ΔT.	M′ΔT/*g.*	*g.*	ΔT.	M′ΔT/*g.*
		26·2			26·9
1.20	·175	26·0	1·22	·139	25·8
2·42	·342	25·2	2·44	·275	25·4
2·82	·408	25·8	4·91	·517	23·8
4·78	·658	24·5	9·93	·957	21·8

SOLUTIONS IN ALCOHOL.

Urea M′ = 60.			Salicylic Acid M′ = 138.		
g.	ΔT.	M′ΔT/*g.*	*g.*	ΔT.	M′ΔT/*g.*
		11·3			11·5
1·32	·245	11·1	1·37	·122	12·3
2·44	·435	10·7	2·76	·229	11·5
2·63	·478	10·9	5·29	·434	11·3
2·64	·478	10·9	8·91	·722	11·2
			17·29	1·394	11·1

Influence of concentration.—If ΔT were strictly proportional to g the values of $M'\Delta T/g$ in any vertical column would be the same. For the alcoholic solutions this is practically the case, even up to a concentration of over 17 per cent. for the solutions of salicylic acid. In general, however, as is illustrated by the solutions in benzene, ΔT does not increase as rapidly as the concentration, hence the molecular rise diminishes as the concentration increases. For a few solutions like those of camphor and naphthalene in chloroform the reverse state of things is exhibited, the molecular rise increasing as the concentration increases. These results support the conclusion already stated regarding the validity of Wüllner's law as applied to dilute solutions.

Influence of the chemical nature of the dissolved substance.—Since the values of the molecular rise, for the same dissolved substance, vary to some extent with the concentration, in order to most satisfactorily compare the values given by different dissolved substances, the effect of change of concentration must be allowed for. This is usually done by finding the probable value of $M'\Delta T/g$ for an extremely dilute solution, for according as the solution is more dilute the more closely it may be expected to conform to the ideal laws. A convenient method consists in plotting a curve with the observed values of $M'\Delta T/g$ as ordinates and either the values of ΔT or g as abcissæ. On extrapolating and finding the ordinate corresponding with ΔT or $g = 0$ the probable value is obtained for the molecular rise in an extremely dilute solution. The numbers given at the top of each of the columns headed $M'\Delta T/g$ in the preceding tables are the values thus deduced. With benzene as solvent, although the molecular weights of the two dissolved substances differ considerably and the variation in $\Delta T/g$ is comparatively speaking large, these values for the molecular rise, *viz.*, 26·2 and 26·9, closely agree. The values given by the two alcoholic solutions, *viz.*, 11·3 and 11·5, are also in satisfactory agreement. Unless in the case of a particular class of substances dissolved in certain solvents—associated solutions—to be discussed at a later stage, the

entire work in this part of the subject indicates that at extreme dilution the molecular rise for an indifferent solution depends only on the nature of the solvent.

Influence of the chemical nature of the solvent.—According to equation (9) the molecular rise should be equal to $\cdot 02T^2/\lambda$. Using Schiff's value for λ, *viz.*, 93·4 cal. and T = 273 + 80·3, the theoretical value of the molecular rise for benzene is 26·7, which is not far removed from those given above. For alcohol, using Regnault's value, 214·9 cal. for λ and 273 + 78·3 for T, the value of $\cdot 02T^2/\lambda$ is 11·5, which again closely agrees with the numbers obtained from the rise in the boiling-point. The following table contains the mean values to the nearest degree of $M'\Delta T/g$ at extreme dilution as deduced by Beckmann (1890) from observations on different dissolved substances in the solvents named, and also the corresponding values of $\cdot 02T^2/\lambda$ as calculated from the absolute boiling-point and heat of vaporisation.

Solvent.	$M'\Delta T/g$.	$\cdot 02T^2/\lambda$.
Water	4-5	5·2
Alcohol	10-12	11·5
Acetone	17-18	16·7
Ether	21-22	21·1
Carbon Bisulphide . .	22-24	23·7
Acetic Acid . . .	25	25·3
Ethyl Acetate . . .	25-26	26·0
Benzene	25-27	26.7
Chloroform . . .	35-36	36·6

The agreement between the two sets of numbers is a satisfactory proof of the validity of the expression—

$$M'\Delta T/g = \cdot 02P^2/\lambda.$$

Boiling-point and gaseous laws.—This equation corresponds, therefore, with the results of experiment, and like Raoult's vapour-pressure relationship which was employed in its theoretical deduction, it furnishes an indirect proof that gaseous laws are applicable to dilute solutions.

If p be the vapour-pressure of the pure solvent at its absolute boiling-point T, and p' the vapour-pressure of

the solution at its absolute boiling-point T_1, by the method which is employed in deducing (8) it may be shown that $\log_e p/p' = M\lambda\,\Delta T/2TT_1$ (10). Here it is assumed since ΔT is small that λ is the same at T as at T_1. ΔT is thus connected with the vapour-pressures of the solvent and solution. Now, equation (6) can give us at T_1 the relation between vapour-pressure and osmotic pressure, hence from (10) and (6) we have—

$$P = \cdot 0819\ \rho\lambda\Delta T/2T \qquad (11).$$

It is thus possible to calculate the osmotic pressure of a solution from the rise in the boiling-point. If we next introduce into (11) the value of λ derived from $M'\Delta T/g = \cdot 02T^2/\lambda$ we have—

$$P = \cdot 0819\ T\rho g/100\ M' \qquad (12).$$

If V be the volume of solution containing M' grams of dissolved substance $V = 100\ M'/\rho g$, the densities of solvent and solution being supposed to be the same, and the weight of the dissolved substance being neglected. Consequently (12) reduces to—

$$PV = \cdot 0819\ T.$$

Observations on boiling-point like the direct observations on vapour-pressure lead, therefore, to the result that osmotic pressure obeys gaseous laws and is independent of the nature of the solvent.

J. W. RODGER.

(*To be continued.*)

ITALIAN ANTHROPOMETRY.

DR. RIDOLFO LIVI still carries on the work of utilising the Italian military statistics for anthropological purposes. His investigation of the cephalic index,[1] a few years ago, resulted in the partial confirmation of the previous work of Calori and Lombroso. Livi showed that the proportion of breadth to length of head in the living man gradually decreased from the north to the south of Italy, being about eighty-eight in the province of Ivrea (Piedmont) and seventy-seven in those of Cosenza (Calabria) and Sassari (Sardinia), the most conspicuous exception to the rule being the comparative longheadedness of the people of Lucca and Liguria.

Already in 1884 Dr. Livi had published the results of an investigation of the comparative stature of Italian conscripts from the several provinces, the most notable conclusion being that the mean stature was highest in Venetia and lowest in Sardinia and Calabria.[2] In his latest publication[3] he has followed the same line of inquiry, but with a much broader basis and with much more minuteness of detail. He has also brought into comparison with the variations of stature in the conscripts those of the complexional characters, the colours of the hair and eyes.

On the first glance at his elaborate maps, one is disposed to conclude that high stature, breadth of head, and blond complexion go together in Italy, and that they abound in the north, while the opposite characters, low stature, long and narrow head, and dark hair and eyes, greatly predominate in the south. A more careful examination somewhat qualifies this impression, and shows us that the case is not quite so simple as one might have supposed. Thus Sicily, the most southern province, stands above Calabria and

[1] *L'indice cefalico degli Italiani.* Firenze, 1886.

[2] *Sulla statura degli Italiani, studio statistico, antropologico.* Firenze, 1884.

[3] *Saggio dei risultati antropometrici ottenuti d'allo spoglio dei fogli sanitarii delle classi,* 1859-1863. *Voghera.* Roma, 1894.

Sardinia in breadth of head as well as in stature and in blond coloration. And Liguria, which, in accordance with its geographical position, stands third in order of stature and fourth in that of colour, is tenth among the provinces in the scale of brachycephaly. It may be as well to give the complete scale, though as regards the cephalic index it cannot be relied on so confidently as in its other departments, as the number of heads measured, though actually very large, was relatively small :—

ORDER OF THE PROVINCES IN RELATIVE

A. Breadth of Head.	B. Stature.	C. Blond Complexion.
1. Piedmont	Venetia	Venetia
2. Emilia	Tuscany	Piedmont
3. Venetia	Liguria	Lombardy
4. Lombardy	Lombardy	Liguria
5. Umbria	Emilia	Tuscany
6. Marches	Piedmont	Umbria
7. Tuscany	Latium	Marches
8. Abruzzi	Umbria	Emilia
9. Campania	Marches	Abruzzi
10. Liguria	Sicily	Latium
11. Latium	Apulia	Campania
12. Basilicata	Campania	Apulia
13. Apulia	Abruzzi	Basilicata
14. Sicily	Calabria	Sicily
15. Calabria	Basilicata	Calabria
16. Sardinia	Sardinia	Sardinia

It is evidently necessary to go more into details. When we do so, we find that the district of Aosta, among the Alps, is the one in which the cephalic index attains its maximum (89). It is also one of the only two in the kingdom in which blond hair is more frequent than black, the other being Domo d'Ossola, which is thought to have been extensively Germanised. In stature, however, Aosta scarcely attains the average of Piedmont; in fact, owing probably to the frequency of goitrous degeneration, it furnishes a large number of undersized men.

Castelnuovo di Garfagnana (a sub-district of Massa, in the Apennines), furnishes a striking contrast. It stands first among the districts of Italy in order of stature (1662 mm.), but is very near the bottom of the scale of brachy-

cephaly (78·8), while as regards complexion it does not deviate much from the average. Conterminous with it is the district of Lucca, second in order of stature, low in the scale of brachycephaly (79·8), and in colour darker than its neighbours. Udine, Vicenza, Chiavari, all very high in stature, all inclining to be blond, are diverse in headbreadth; in the two former the heads are broad, in the latter only moderately so. Pontremoli, Gallarate (Milan), Varese, Borgotaro (south of Parma), Guastalla, Pistoja, Perugia, Civita Vecchia, and the neighbourhood of Benevento (the ancient Samnium) are rather fair in comparison to their neighbours. And, generally speaking, the frontiers where Italy is in contact with the French, the Swiss, the Slavs, furnish the largest proportion of blonds. The lowest proportion is found in the district of Lanusei, Sardinia, in company with the lowest mean stature.

On the whole, ethnological history, or ethnic movements prior to history, furnish the only adequate explanation of these eccentricities. Not that there are simply two races, one in the north, tall, brachycephalic and comparatively blond, and one in the south and the islands, short, long-headed and very dark; but that a type, the one we usually call the Mediterranean, and having these latter characteristics, does really predominate in the south, and exists in a state of comparative purity in Sardinia and Calabria, while in the north the broad-headed Alpine type is powerful, but is almost everywhere more or less modified by or interspersed with other types, Germanic, Slavic, or of doubtful origin, to which the variations of stature and complexion may probably be, in part at least, attributed. In Sicily, Greek, Carthaginian and Saracenic settlements and invasions have doubtless had considerable modifying influence.

Dr. Livi has, however, done much in the way of investigation of the effects of media and surroundings on physical type.

He finds that the stature varies, on the whole, inversely with the elevation of the country, and this is the case when one divides the several districts into four categories, one at less than 50 metres above the sea, one at from 50 to 200

metres, one at from 200 to 400, and one at upwards of 400 metres. At much higher elevations (over 900 metres) the case is not so clear; but the number of recruits coming from these very lofty tracts is perhaps insufficient. It is, however, somewhat disappointing to find that these variations depend not purely on the elevation, but partly on the geographical position of the districts, *i.e.*, that the low-lying districts are in very large proportion situated in the high-statured areas of the north, the mountainous ones in the short-statured areas of the south and of the islands, or, in other words, that at the different levels we are to a large extent dealing with different races. Thus, Venetia, where the stature is highest, has only 5 per cent. of its population in districts whose chief towns are more than 400 metres above the sea-level; while Basilicata, the ancient Lucania, has 86 per cent., the Abruzzi 65, Umbria 64, Sicily 43 and Sardinia 32 per cent. When the rule is tested by its application to the sixteen provinces separately, we find that only ten of these conform to it, one (Piedmont) being neutral, and five following the opposite rule. These five are Venetia, where, as has been stated, almost the whole of the population dwells on a low level, and Basilicata, Umbria, Abruzzi, where the majority, and Sardinia, where a third, of the inhabitants are above the 400 metre line. If Dr. Livi's opinion be correct, that the low stature of the mountaineers is due to poverty and insufficient food, these exceptions to the rule might probably be accounted for with the help of a better knowledge of the local social and sanitary conditions.

With a view to testing his opinion, Dr. Livi has further ascertained the differences in stature between the students and upper class conscripts and the peasants, in the districts of the sixty-nine chief towns. The result is pretty much as might have been expected. In sixty-eight of these districts there is a larger proportion of tall students (over 1700 mms. or about 67 inches) than of tall peasants; and in sixty-three there is a larger proportion of short peasants (under 1600 mms. or 63 inches) than of short students. The mean stature of these two classes is not given, so that it is not possible to ascertain the average difference between them,

but while in eight cases the students attain a mean of 67 inches or more, there are forty-two out of the whole number of districts (which is 206) in which the mean stature of the entire male population (including all the rejected), at twenty years of age, does not exceed 1600 mms. or 63 inches. The whole of these forty-two are situated either in the island of Sardinia or within the limits of the old kingdom of Naples, and nowhere else in Europe, so far as we know, can such a mass of undersized people be met with. The average for the entire kingdom is 1624 mms. or about 64 inches. This is much below that of most parts of Northern and Central Europe, though perhaps equal to that of Poland and of Central Hungary. And it is considerably below that of the conterminous countries, France, Switzerland, Austria and the Hungarian Littoral, though not below that of every French department or of every Swiss canton.

An interesting and extensive investigation of the circumference of the chest has the following results :—

1. The *absolute* chest-measure increases directly with the stature, but

2. The *relative* magnitude increases inversely as the stature.

3. In the kingdom taken as a whole, and in twelve of the sixteen provinces, the chest-measure is a little larger in the mountaineers than in the inhabitants of the plains, for equal statures.

4. The chest-measure is, not only absolutely, but apparently also in relation to the stature, comparatively small in the extreme south and in the islands ;

5. And comparatively large in Lombardy, Liguria, Emilia, Umbria, Latium and Apulia.

The larger chest-circumference of the mountaineers may be due, as Livi supposes, partly to the greater rarefaction of the air at high levels, but partly to the facts that the mountaineers are mostly agricultural or pastoral by occupation, and that there are few considerable towns situated at a high level. As for its relation to racial differences, it is generally believed, as much perhaps from common observation as from the more definite authority of Collignon and Houzé,

that the brachycephalic Alpine race (the Keltic of Broca) is proportionally larger-chested than the northern dolichocephals; and from the facts just now detailed, one might feel disposed to say that it was equally superior in this respect to the southern or Mediterranean dolichocephals. There are, however, unexplained anomalies, such as the superiority of Apulia to Piedmont, which must prevent our asserting this positively.

As for the local distribution of blonds and brunets, it would seem that there is no very material difference at the several elevations tested. If there be any, it consists in this, that light eyes and hair are a little more frequent between the levels of 50 and 400 metres, and a little less so in the mountains, and in the plains near the level of the sea. Unfortunately, in this case as in that of stature, the value of the result is somewhat impaired by the fact that the several provinces vary so widely in their partition between the different levels. Dr. Livi affords us some material for a comparison of the high and low levels of the several provinces respectively. Examining, however, his beautiful maps with what light one has on the hypsometry of the country, one cannot help having a suspicion that elevation, acting through natural selection, may have something to do with the greater prevalence of xanthosity in the following cases:—

1. Vicenza, the most blond district of the Venetian province. It is true that it contains the Germanic or semi-Germanic sub-district of the Sette Communi.

2. Sondrio, Domo d'Ossola, and most of the other Alpine districts of Piedmont.

3. Borgotaro, an upland sub-division of Parma.

4. Portions of the ancient Samnium.

The cities have generally considerable rural districts attached to them, which renders it difficult to appreciate the special effects of urban life upon the physique. These are nowise conspicuous. In some cases the town population appears a little darker, in others a little lighter than that of the surrounding country. The stature seems to me to be, if anything, rather higher in the great towns, with the ex-

ception of Milan and Venice. The towns no doubt contain a larger proportion of the upper and well-nourished classes; the poverty of the Italian peasantry is notoriously great, so that this superiority in mean stature of the townspeople might have been expected. Quetelet long ago[1] showed that in Brabant, at conscription ages, this superiority existed, and Ammon[2] has demonstrated it in Carlsruhe and Freiburg-in-Brisgau; but it remains uncertain whether the inferiority of the peasantry may not be due merely to retarded development, and whether it may not wholly disappear before the completion of growth, or, say, by the twenty-fifth year. As for coloration, Virchow's great inquest into that of the German school children, and George Mayr's publication on the same subject, as well as my own observations on British adults, point to the existence of a majority of much-pigmented people in towns as compared with rural districts, whatever may be the causes of the phenomenon; but these Italian statistics do not, so far as published, appear to carry us any farther.

Another important department of anthropometry, that of the effect of pathological conditions on the stature, has been well handled by Livi, who has some very pregnant material wherewith to deal in the figures relating to districts infested with goitre, malaria, and pellagra.

Of these three deteriorating causes, the first, though it may not, perhaps, be quite so widely diffused throughout the kingdom as the second, is vastly more powerful in its own domains. In Aosta, the district which stands worst in this respect, and which, as we have noted, stands at the head of the lists of brachycephaly and fair complexion, the number of young men rejected for goitre, during the period 1863-76, was no less than 31·7 per cent.,[3] and this was after 26·7 per cent. had been rejected for deficient stature; for in Italy measurement precedes medical examination of the conscripts. Of these 7·1 had a stature

[1] Quetelet, *Anthropometrie.* Brux, 1870.

[2] Ammon, *Naturliche Auslese beim Menschen.* Jena, 1893.

[3] Sormani, *Geographia Nosologica d'Italia. Annal. di stat.* Roma, 1877.

of 145 mms. (57·1 inches) or less. There can be no doubt that a great part of those thus rejected for deficient stature, probably the majority of them, were also goitrous, but Dr. Livi contents himself with the moderate estimate that 40 per cent. of the young male population are thus afflicted. The effect of this in lowering the average stature of the recruits presented for examination is great, so great that their average stature in Aosta is only 1603 mms. (63·1 inches), which is simply identical with that in the district of Cosenza, among the dwarfish Calabrians. Yet the *type* of stature, as Livi calls it, the stature, that is, as determined by what we call race or heredity, and exhibited by healthy persons, is comparatively tall. The curve of stature, though beginning very early, and rising irregularly with many oscillations, does not actually culminate below 1650 mms. (65 inches), whereas that of Cosenza culminates somewhere about 1600 mms. (63 inches). And the percentage of tall men (1700 mms.) among the soldiers from Aosta is 19·5, about the average of Piedmont, and of short men (under 1600 mms.) 18·1, whereas the figures for Cosenza are 11·5 and 23·2.

Livi carries on the comparison, matching other pairs of districts, healthy with unhealthy, goitrous with non-goitrous, as Sondrio with Benevento, and Clusone with Foligno. The results are strictly analogous; and he shrewdly remarks that the previous rejection of the pathologically dwarfish or diseased leaves behind a mass of material all the better fitted for investigation into the influences of race and media.

The effects of malaria and of pellagra on the stature are much more difficult to ascertain. Livi singles out the district of Grosseto, on the low, marshy coast of Tuscany, as probably the most malaria-infested in the whole country; but there is nothing very remarkable therein as to stature or complexion, and the proportion of conscripts rejected is below the average of the kingdom! There is room here for further investigation. One has heard or read much about physical degeneracy in fever-stricken districts like the Sologne, but countervailing examples may easily be found, such as the proverbial beauty and fine development of the

people of Arles. Pellagra again, though still widely diffused in the region of the Po, is difficult to identify in the statistics as a cause of degeneration; it is seldom mentioned as a cause of disqualification.

Livi is an accomplished handler of statistics, and is quite aware of their weak points, such as the propensity of observers to choose a round number rather than the one immediately below or above it, and even to treat numbers with a 5 in the unit place as round numbers. It is on grounds such as these that he ventures to challenge the applicability of the law of the bicipital curve, discovered by the elder Bertillon, to many of the cases which are cited as examples of it. For, says he, when you amalgamate the curves representing the stature of two races differing by not more than 6 or 7 centimetres (provided that these curves are tolerably uniform and free from the effects of the tendency to round numbers and otherwise incorrect observation) there will result not a double vertex but simply a broadening and a depression of the upper part of the figure. This he exemplifies by amalgamating the curves of Udine, in the Frioul, and Oristano, in Sardinia, the average stature of these districts being 1657 and 1585 millimetres respectively. The resultant curve is broad and flat. with but a slight appearance of duplicity. But when Livi goes on to imply that the double peak in the curve of the Doubs, which suggested the idea of two races to Bertillon, is probably due to the grouping of the measurements by inches instead of centimetres, to the idolatry of round numbers or to similar causes, I think he goes a little too far. Lagneau[1] has shown that the phenomenon in question is equally well or even better marked in the Oise, the Seine-Inferieure and several other departments of the north and north-east of France, precisely where the history of Gallic and Germanic conquest would lead us to expect it, while in the more purely Keltic portions of France it does not appear.

[1] *Anthropologie de la France*, p. 41. Paris, 1879.

JOHN BEDDOE.

THE MOST RECENT VALUES OF THE MAGNETIC ELEMENTS AT THE PRINCIPAL MAGNETIC OBSERVATORIES OF THE WORLD.

[Through the courtesy of the Kew Committee of the Royal Society and of Mr. Chree, the Superintendent of the Kew Observatory, arrangements have been made for the publication, in this journal, of a table showing the mean annual values of the magnetic elements as determined at the various magnetic observatories of the world. It is intended that this table shall appear about July in each year.—ED.]

THE phenomena of terrestrial magnetism possess so many points of interest that in a short article it is only possible to glance at a portion of the field. The magnetic phenomena at any one place show, as is well known, a continual fluctuation. There is a general drift, or secular variation, proceeding in the same direction for many years, together with more or less regular annual and diurnal variations and probably other minor oscillations of a cyclic character. There are also numerous irregularities, which when sufficiently intense are dignified with the title of *magnetic storms.*

To analyse the phenomena it is necessary to consider separately the various magnetic *elements.* Three elements, two being angles measuring direction and one a measure of intensity, suffice to define the magnetic force. It is customary and more convenient, however, to record the intensity not of the whole force but of its *horizontal* and *vertical* components. The usual angular elements are the *declination,* or angle the horizontally suspended magnetic needle makes with the geographical meridian, and the *inclination,* or *dip,* which is the angle made with the horizontal plane by a magnetic needle freely movable in the magnetic meridian.[1]

One of the fundamental objects of magnetic observations is to supply the data required for the construction of maps, or

[1] The magnetic meridian is the vertical plane which contains a freely suspended horizontal magnet.

charts, showing the simultaneous values of the several magnetic elements over the whole or a portion of the globe.[1] Such maps may be divided into two classes, *viz.:* (1) maps on which the values of the declination are indicated with sufficient accuracy for the requirements of travellers by land or sea, (2) maps (up to the present almost exclusively of land) on which the values of the magnetic elements are given with all possible precision. The latter class is chiefly of scientific value, as showing the relations between the magnetic and geological constitution of the districts surveyed, and giving information on other similar points. It is hardly perhaps apparent at first sight that the successful construction of these maps is largely dependent on the existence of fixed magnetic observatories keeping a record of magnetic history; such, however, is the case, as the following considerations will show. Maps of the first class, however, if correct when drawn, would soon be useless unless allowance were made for the secular change of declination. The necessary data are partly supplied by observations made at sea, but as these are not very accurate it is most important that they should be confirmed by more exact work at numerous magnetic observatories. In the construction of maps of the second kind magnetic observatories play a still more important part.

Exact magnetic observations can only be taken by highly trained observers with first-class instruments, and without an enormous expenditure it is impossible to multiply largely either observers or instruments. Thus the carrying out of a magnetic survey over a large area is a work not of days but years, and the data obtained for constructing a chart refer to such different times that allowance must at least be made for the secular variation of the elements.

Again the diurnal variation in some of the elements is very considerable. At Kew, for instance, on an average the declination magnet points eight minutes of arc further to the westward at 2 P.M. than it did six hours previously.

[1] *Cf.* Captain Creak's *Report on the Magnetical Results of H.M.S. "Challenger"*.

Thus when, as usually happens, observations of an element are taken at times other than those at which it just attains its mean daily value, allowance should be made for the diurnal inequality. Finally, irregular fluctuations in the magnetic elements are not infrequent. Occasionally these are very large; for instance, Professor Adams in the *Philosophical Transactions* for 1892, p. 136, refers to a rapid change of over fifty-three minutes of arc as occurring on one occasion in the declination at Toronto. In such an exceptional case, of course, a careful observer would almost certainly detect the existence of a severe magnetic storm. Usually, however, irregular fluctuations are neither so sudden nor so large as to betray their existence to an observer on a survey, as he has not the proper instruments for dealing with them. The ideal arrangement, no doubt, would be to have instruments giving a continuous magnetic record at all the places where absolute observations are taken, but the expense is prohibitive, and fortunately the case is fairly met by a comparatively small number of fixed observatories. The secular variation, the diurnal inequality, and, as a rule, even the irregular fluctuations, present very similar features over a large area.[1] The curves showing the fluctuations recorded by instruments of the same pattern at two observatories within a few hundred miles of one another are closely similar. If the disturbances are large and sudden it would perhaps be hardly prudent to rely on the records of a distant observatory for particulars. But even then these records might prove of no inconsiderable use indirectly in checking the fancy of an observer when working up his results.

To enter on details with respect to the magnetic records for one year of even a single observatory would occupy too much space. It is possible, however, to supply in brief compass a table of the mean annual values of the elements at a number of observatories, and this is done here with the hope that it will prove both useful and interesting. In one

[1] *Cf.* Professor W. G. Adams, *B. A. Reports*, 1880, p. 201, and 1881, p. 463, also Mr. W. Ellis, *Proceedings of Royal Society*, vol. lii., p. 191, 1892.

or two cases the information has been courteously supplied in answer to special application, by directors of observatories whose publications were not accessible, but it has mainly been extracted, with the sanction of the Kew Committee of the Royal Society, from the official publications received by the Kew Observatory. Few of these publications can be consulted except by those who have access to a good library, and frequently mean annual values are not explicitly given but have to be deduced by more or less arduous calculations. The numerical measures of force are all given here in terms of C. G. S. units, measurements in terms of British units having been transformed when necessary.

Taking a well-equipped magnetic observatory, we find two distinct sets of observations in progress. There are, first, the absolute observations, in which numerical values of the declination, dip and horizontal force are obtained at intervals from direct observations. There are, secondly, the magnetic curves from the self-recording instruments, called magnetographs, which supply a practically continuous record of the variations in the values of the declination and the horizontal and vertical forces. The curves by themselves supply a large amount of qualitative and even to a certain extent of quantitative information, but for the deduction of a satisfactory value for such a quantity as an annual mean they must be standardised by the aid of the absolute observations.

In a magnetic curve distances in one direction, taken as abscissæ, measure the time, while distances in a perpendicular direction, taken as ordinates, give the differences of the magnetic element considered from a certain value answering to the base line. The value of unit length of the ordinate is obtained by direct experiments performed, say once a year, on the magnetographs. The determination of the value of the element answering to the base line is effected by measuring the ordinates corresponding in time to the absolute observations, and for various reasons it is expedient to make this comparison pretty frequently.

When the magnetic curves have been standardised they may be employed to get the diurnal oscillation and mean

values for the month or year. For this purpose use may be made of the curves of every day in the year, or of every day free from serious disturbance, or of any smaller number of days that may be deemed sufficient. At some observatories, as at Greenwich, measurements are taken for every hour, at others for every sixth, at others for every eighth hour, and various other plans are elsewhere in vogue.

The operation of taking measurements for every hour of every day unfortunately entails a very large amount of labour and may also distort the average diurnal oscillation with the effects of magnetic storms which are not uniformly distributed over the twenty-four hours. This led Professor Wild of St. Petersburg, many years ago, to suggest the restriction of the hourly measurement to the curves for a comparatively small number of *quiet* days, or days of no appreciable disturbance, selected by actual inspection. The adequacy of five quiet days a month for most purposes seems indicated by independent researches of Professor Rücker[1] and the late Mr. Whipple.[1] This number has met with the approval of the Magnetic Committee of the British Association, and to secure uniformity the Astronomer Royal has undertaken to choose from inspection of the Greenwich curves the most suitable quiet days and to communicate these to other observatories. At present the observatories at Falmouth and Kew employ these days alone for their monthly and annual means, whilst at Greenwich special tables for these days are constructed in addition to the more complete tables.

Mean annual values deduced from the magnetic curves are the most satisfactory when obtainable, but unfortunately a good many observatories furnished with magnetographs do not state them explicitly in their publications. In some of these cases data are given from which mean annual values may be calculated, but in other instances this does not appear to be the case. Not unfrequently results are stated in terms of arbitrary scale divisions, whose values are not given in the publication of the year under consideration. Research into the publications of previous years may lead

[1] See *B. A. Report* for 1890, p. 172.

Place.	Latitude.	Longitude.	Year.	Declination.
Pawlowsk (near St. Petersburg)	59° 41′ N.	30° 29′ E.	1892	0° 1′·0 W.
Copenhagen . .	55° 41′ N.	12° 34′ E.	1892	10° 53′·1 W.
Stonyhurst . . .	53° 51′ N.	2° 28′ W.	1893	18° 46′·5 W.
Hamburg . . .	53° 34′ N.	10° 3′ E.	1893	11° 54′·3 W.
Wilhelmshaven . .	53° 32′ N.	8° 9′ E.	1892	13° 10′·1 W.
Kew	51° 28′ N.	0° 19′ W.	1893	17° 28′·8 W.
Greenwich . . .	51° 28′ N.	0° 0′	1893	17° 11′·4 W.
Falmouth . . .	50° 9′ N.	5° 5′ W.	1892	19° 13′·1 W.
Prague . . .	50° 5′ N.	14° 25′ E.	1892	9° 48′·6 W.
Parc St. Maur (near Paris)	48° 49′ N.	2° 29′ E.	1891	15° 32′·8 W.
Vienna . . .	48° 14′ N.	16° 20′ E.	1890	9° 5′·9 W.
Buda Pesth . .	47° 30′ N.	19° 2′ E.	1888	8° 7′·2 W.
Pola (on Adriatic) .	44° 52′ N.	13° 50′ E.	1893	9° 57′·3 W.
Perpignan . . .	42° 42′ N.	2° 53′ E.	1891	14° 21′·4 W.
Rome . . .	41° 54′ N.	12° 26′ E.	1891	10° 45′ W.
Tiflis (Transcaucasia) .	41° 43′ N.	44° 48′ E.	1891	1° 27′·9 E.
Coimbra . . .	40° 12′ N.	8° 25′ W.	1892	17° 57′·4 W.
Washington . .	38° 53′ N.	77° 0′·0 W.	1890	4° 5′·8 W.
Lisbon . . .	38° 43′ N.	9° 9′ W.	1888	18° 16′·4 W.
Los Angeles (California)	34° 3′ N.	118° 15′ W.	1889	14° 22′·9 E.
Zi-ka-wei (China) .	31° 12′ N.	121° 26′ E.	1892	2° 14′·4 W.
Hong Kong . .	22° 18′ N.	114° 10′ E.	1892	0° 33′·5 E.
Colaba (Bombay) .	18° 54′ N.	72° 49′ E.	1892	0° 42′·7 E.
Manila (Philippines) .	14° 35′ N.	127° 11′ E.	1891	0° 49′·7 E.
Batavia . . .	6° 11′ S.	106° 49′ E.	1892	1° 34′·8 E.
Loanda (West Africa) .	8° 48′ S.	13° 14′ E.	1888	18° 9′·1 W.
Mauritius . . .	20° 6′ S.	57° 33′ E.	1892	10° 5′·1 W.
Melbourne . . .	37° 50′ S.	144° 58′ E.	1891	7° 58′·5 E.

Place.	Year.	Inclination.	Horizontal Force.	Vertical Force.
Pawlowsk . . .	1892	70° 45′·1 N.	·16424	·47037
Copenhagen . . .	1892	68° 50′·4 N.	·17334	·44782
Stonyhurst . . .	1893	69° 2′·6 N.	·1716	·4479
Hamburg . . .	1893	67° 45′·4 N.	·18003	·44022
Wilhelmshaven . .	1892	67° 57′·3 N.	·17917	·44245
Kew	1893	67° 26′·3 N.	·18238	·43896
Greenwich[1] . . .	1893	67° 18′·9 N. 67° 17′·8 N.	·18287	·43747 ·43708
Falmouth . . .	1892	67° 7′·1 N.	·18443	·43686
Prague	1892	—	·19754	—
Parc St. Maur . .	1891	65° 10′·1 N.	·19558	·42266
Vienna	1890	63° 17′·2 N.	·20641	·41036
Buda Pesth . . .	—	—	—	—
Pola	1893	60° 39′·6 N.	·21988	·39117
Perpignan . . .	1891	60° 15′·3 N.	·22249	·38936
Rome	1891	58° 4′·6 N.	—	—
Tiflis	1891	55° 43′·7 N.	·25714	·37735
Coimbra . . .	1892	59° 53′·2 N.	·22477	·38753
Washington . . .	1890	71° 4′·5 N.	·19860	·57928
Lisbon	1888	58° 37′·3 N.	·23086	·37853
Los Angeles . . .	1889	59° 29′·0 N.	·2725	·4630
Zi-ka-wei . . .	1892	46° 7′·0 N.	·32500	·33792
Hong Kong . . .	1892	32° 3′·5 N.	·36352	·22767
Colaba	1892	20° 33′·3 N.	·37424	·14033
Manila	1891	17° 16′·3 N.	·37616	·11697
Batavia	1892	28° 58′ S.	·37125	·20551
Loanda	—	—	—	—
Mauritius . . .	1892	54° 48′·2 S.	·24003	·34030
Melbourne . . .	1891	67° 12′·1 S.	·23475	·55856

[1] First results from 3 inch dip needles only, second mean from 3, 6 and 9 inch needles.

to the discovery of a scale value, but this cannot be trusted to for absolute results in view of the change that has probably occurred. In such cases it seems preferable to employ the records of the absolute observations, and in some observatories these are the only results obtainable. Absolute observations, if a sufficient number exist, are satisfactory enough, when corrected for the diurnal inequality. In some instances where no such correction seems to have been applied, the hour or hours of observation may have been chosen so as to eliminate the inequality. Unfortunately information on this point is commonly deficient, and it might be as well in such cases to regard the results as uncertain to the extent of at least half the daily range.

This uncertainty is in reality not so serious a matter as might appear at first sight, for observatories as a rule are so conservative in their instincts that their results for successive years, though possibly in strictness not mean annual values, are fairly comparable amongst themselves. The uncertainty arising from possible differences between the instruments at different observatories has also to be kept in view. An interesting example bearing on this point is furnished by the Greenwich results in the table for dip needles of different lengths.

In the publications of most magnetic observatories force is measured to five significant figures, and declinations and dips to the nearest tenth minute, and when this is done the practice has been followed in the present table. After the warning given above as to probable differences between the instruments at different observatories this can do no harm, and it may prove useful in tracing secular variation if similar tables be published in future years.

The interval elapsing before the publication of results varies much in different observatories, so that there is unfortunately a considerable variety in the dates in the table. Following the example of the *B. A. Report* for 1887, pp. 328-331—a source from which a good many of the geographical data are taken—I have arranged the observatories according to their latitude. The longitude is in all cases referred to Greenwich. In some few cases where the geo-

graphical position had to be extracted from a map, and in others where conflicting statements existed, there may not unlikely be appreciable error.

The data in the table are deduced from hourly readings of the magnetic curves in the case of Pawlowsk, Copenhagen (April—December only), Kew, Greenwich, Falmouth (declination and horizontal force), Parc Saint Maur, Pola, Perpignan, Tiflis, Washington, Zi-ka-wei, Manila, Batavia and Mauritius (?). In the case of Hamburg (declination), Wilhelmshaven, Vienna (declination and horizontal force), Prague, Coimbra (declination), Lisbon (declination), Hong Kong and Colaba (all elements but declination) the diurnal inequality has been at least partly, in some cases probably with great exactness, allowed for by taking readings from curves or absolute instruments at two or more different hours. In other cases the hour selected for observing a particular element may more or less accord with the time at which it has its mean daily value, but information on this point is lacking. In a few cases, *e.g.*, Rome, where regular magnetic work seems only commencing, the recorded observations are perhaps somewhat few to supply a satisfactory annual mean.

CHARLES CHREE.

ON THE SUCCESSION AND GENESIS OF MAMMALIAN TEETH.

THE form and relations of the teeth have always occupied a prominent place among those characters which determine the systematic position and individual peculiarities of any mammal. And when we consider that owing to its composition a tooth is one of the most resistant structures which these animals possess, it will at once be evident that the importance of the teeth cannot be overestimated in relation to the study of the past history of the group as determined from their fossil remains. We cannot therefore investigate too carefully the many doubtful points in tooth relationships, the solving of which may assist us in obtaining a more complete knowledge both of the inter-relationships of the different orders of mammalia and of the ancestry of the mammalian phylum itself.

The study of comparative odontology is a very old one, but it is not until we come to the beginning of the present century that we find any very comprehensive attempt to treat this subject in a systematic way. Such an attempt we owe to F. Cuvier (1), who was one of the first to give us any detailed description of the teeth of a large number of mammals and to endeavour to homologise the same.

Following closely upon Cuvier we find Owen (2, 3, 4, 5) in this country working at the same subject, and it is from his numerous memoirs that the science of comparative odontology may be said to have arisen. On comparing his results with those of more recent investigators, it is astonishing to find how very little our latest conclusions differ from those at which he arrived as early as 1868, especially when we consider the advances which have been made in the methods of observation.

His introduction (5) of a systematic method of expressing the dentition of a mammal by means of symbols has been of immense use to comparative anatomists, although the use of these dental formulæ may be in some instances carried too far, considering that they may only

represent the apparent or physiological, and not necessarily the true, relationships between their component teeth.

A very interesting paper published in 1868 by Lankester and Moseley (47) criticised these views of Owen's and suggested, with a good show of reason, a new system of nomenclature, which although of great interest has never been adopted.

Owen's subdivision of the mammalian dentition into two types, the *monophyodont* and *diphyodont*, implying respectively the presence of one set only or two sets of teeth, has endured until quite recently, although it was shown as long ago as 1869 by Flower (6) that this generalisation was incorrect.

His views as to the relation of the milk and replacing teeth vary considerably in his earlier and later works; thus we find him at one time stating that the marsupials possess milk incisors which are shed early in life, while in his latest works he says (4, p. 379) that the functional incisors, canines and deciduous molars of these animals are possibly to be referred to the first or milk dentition;[1] this, taken in conjunction with another statement which he makes (4, p. 368), *viz.*, that "the molars are a continuation backwards of the primary or milk series," shows that Owen in 1868 anticipated those views put forward as original in the last few years by various continental observers, which have received such universal acknowledgment.

Next to Owen in this country we are indebted to Flower for a great advance in our knowledge of this subject; the latter was the first to study the fœtal dentition in the flesh, and he by this means definitely determined the exact number of replacing teeth in the marsupials (7). From the study of the relations of the two dentitions in those animals

[1] The detailed description which Owen gave of the shedding of the supposed milk incisors (3, 5) leads one to think he must have had some evidence to go upon in making this statement. Recently I have described the presence of some additional vestigial incisors in *M. major* (12), and it seems just possible that Owen may have come across specimens in which these were abnormally developed and mistaken them not unnaturally for the deciduous incisors. His sudden change of opinion may have been due to the appearance of Flower's investigations (7) although he does not refer to them.

and especially from the tooth change in *Thylacinus*, Flower put forward the theory that the persistent teeth in the marsupials corresponded with the second dentition of the placentalia, and that the milk teeth of the latter were a secondary set superadded to the permanent ones and represented in marsupials by a single tooth only, the "third" (fourth) deciduous premolar. He further sought to demonstrate (6) that the homodont dentition of the cetacea was homologous with the second or replacing dentition of the more typical mammals. This last conclusion, which has been so long accepted, was deduced from a comparison between the dentitions of the Odontoceti and the Pinnipedia, the latter possessing a very much reduced milk dentition and functional teeth which have a tendency to become homodont.

Those views were accepted in their entirety by Huxley (8), and it was largely due to him that there was first formulated the conception of affinity between the cetacea and the seals (9). The comparison between the dentitions of these forms has been now shown to be misleading (26), as the cetacea possess persistent milk teeth, with which, in some cases, there are said to be fused vestigial replacing ones, while the pinnipedia on the other hand possess a well-developed replacing set, their milk set, even including the molars, being in some forms very much reduced.

Although the belief in the primary nature of the replacing teeth did not attain much support on the continent it met with more success in England; and in 1887 Thomas (10) contributed a very important paper in which he supported this view. In this paper he identified the solitary changing premolar of the marsupials with the fourth premolar of the placentalia and not with the third as had hitherto been generally done, and he showed that it was pm2 which was suppressed in all living marsupials. Four premolars were thus supposed to have been characteristic of the earliest mammals as well as of the later ones. This view was supported by the presence of a replacing tooth under the fourth cheek tooth of *Triacanthodon*, which Thomas demonstrated for the first time. This interpretation, although generally adopted, has been criticised by Cope

(11), who believes that if Thomas' pm2 exists it proves the presence of five, not four, premolars in the marsupials, as he considers with Owen (4) that the first so-called molar of these forms is really the last premolar. Continental observers (26, 32) persist in calling this changing tooth pm3, because they have been unable to find any trace of the missing pm2 of Thomas in the developmental stage. While studying the development of the premolars in the *Macropididæ* (12) I have deduced reason for the belief that the successional premolar is in reality not a replacing tooth but a retarded milk tooth, intermediate in position between pm3 and pm4, and I further discovered the presence of one premolar germ in front of the functional cheek teeth. This would give us four premolars, without counting the first molar as do Cope and Owen.

The condition of this replacing tooth in *Macropus* might well appear to support the theory of Baume (13) that the two dentitions of the mammalia had a common origin in a single set lineally disposed, and that each alternate tooth, owing to the shortening of the jaw, became retarded in its development and displaced so as to be situated below and behind the tooth immediately in front, thus giving rise to the two apparently distinct generations of teeth, the underlying ones eventually pushing out the more superficial set.

This theory might explain to a certain extent the relation of the teeth seen in some reptiles (*i.e.*, *Varanidæ*) and also the case of the premolars of *Macropus* just mentioned, but we have no palæontological evidence which in any way bears out this view in the mammalia and I should rather regard the case above recorded as a feature developed in the marsupials alone, *i.e.*, one in which a milk tooth has simulated the relations of a replacing tooth, and not as one which gives us any real clue to the relations of the milk and replacing dentitions.

All attempts to study the homologies of the individual teeth in different orders of mammalia are very important from a phylogenetic point of view, and we owe much to Thomas (10) for his careful study and suggestions in this direction. Unfortunately even now we know very little of

the development of the teeth in the majority of mammals, and consequently we know next to nothing about the various vestigial teeth, which there is no doubt many of them possess. When Thomas wrote we knew still less, so that it is not surprising to find that many of his generalisations do not hold good. In the case of the incisors I have shown (12) that suppression does not necessarily take place at one end in the series but that it may commence in the middle. His very important discovery (14) of the presence of a milk dentition in *Orycteropus* carries on the work of Gervais, Flower (25), Tomes (24) and others, and shows that the Edentata are truly diphyodont, and that it is their milk dentition which has disappeared. Pouchet and Chabry (15, p. 173), who had previously worked at the *Orycteropus* by means of sections, had described the presence near the symphysis of the lower jaw of a minute calcified tooth and an enamel organ of another tooth behind this; these teeth, which they regard as milk incisors, are anterior to those described by Thomas, and show that these animals originally possessed a complete and probably heterodont dentition.

Another instance in which the microscope has revealed an important discovery of teeth is that described by Poulton (16) of the true teeth of *Ornithorhynchus*, afterwards worked out by Thomas (17) and Stewart (18) in older specimens and shown to be functional. It would be of great interest to re-examine Poulton's sections in the light of recent discoveries, to determine if possible to which dentition these teeth should be referred.

Since Röse's discovery (19) of tooth germs in *Manis* there only remain the *Myrmecophagidæ* and *Echidna* as possible edentulous mammals, and there can be little doubt that even in these animals we shall ultimately find traces of teeth in the young.

On the continent we find that the milk dentition has long been regarded either as the primitive one, or at least equal in antiquity to the replacing set. The latter view was urged by Lataste (20), who considered that the two sets of teeth were inherited direct from the polyphyodont reptiles, and that the mammalia were primarily diphyodont.

The greatest contention has raged round the molars; Lataste (20), maintaining that they belonged to the second dentition, was supported by Magitot (21), whereas Beauregard (22) believed them, as Owen had previously done, to belong to the milk dentition.

Nearly all these views were based on the study of dried skulls or of the relative position of the calcified teeth in the gum of the young animal and not on microscopic study of the relation of the enamel organs to one another, by which alone these points can be cleared up. It is true that Tomes (23) had done a great deal in the microscopy of teeth and that Pouchet and Chabry (15), who had worked in this way at quite a number of mammals, had definitely shown amongst other things the relation of the minute milk incisors of the rabbit to the functional ones; but the last-named investigators did not realise all that their specimens show, for they certainly figure the molar of a squirrel with what would be now regarded as a rudiment of a successional tooth.

Not until the last three years has the microscopic study of the developmental relationship of the sets of teeth occurring in mammals been seriously taken up. Now, however, we are almost flooded with literature on this subject, and in many instances we now are familiar with the development of the teeth from their earliest indication until the distinct sets are fully formed.

The earliest worker in this direction was Kükenthal (26, 27). His chief work (26, 28) deals with the hitherto supposed monophyodont dentition of the whales, which he has shown to be in reality diphyodont, the functional or most developed set being in the Mystacoeti, the remains of the milk dentition. In certain Odontocoeti (*Phocoena*) he considers this to represent a fusion of the two dentitions, the milk set, however, predominating. He confirms the observations of earlier writers as to the primarily heterodont nature of the cetacean dentition and comes to the conclusion that the homodont dentition of these animals is secondary and largely due to a splitting apart of the component conical cusps of the double teeth. In like manner

he has proved the diphyodont condition of the Edentata, and in *Dasypus* he has described three additional anterior vestigial teeth. But he is surely in error when (29, 403-4) he states that the similarity between the dentition of the cetacea, edentates and marsupials is due to the persistence of the first dentition, for the succession, as determined in *Tatusia* by Rapp, Kraus (46), Gervais (36), Flower (25), Tomes (24), and in *Orycteropus* by Thomas (14), shows that it is the milk or first dentition which is transitional, although in the first-named genus it may persist for some time as a series of functional and rooted teeth while the adult dentition is undoubtedly the replacing or second set. In the marsupials (27) he showed for the first time, by the discovery of an almost complete series of rudimentary germs of a second set of teeth, that the permanent dentition with the exception of the one replacing tooth is a persistent milk dentition. He has thus unconsciously revived, after a lapse of twenty years, Owen's conclusions on this question, definitely showing that the milk dentition is not of secondary origin, but at least of equal antiquity with the replacing one; and his ultimate conclusion is that the two sets of teeth are to be regarded as sister dentitions.

Röse (30, 31), who had been working at the development of the teeth in the human subject previous to the appearance of Kükenthal's views, took up this new departure with great energy, and has since published about twenty papers dealing with the detailed development of the teeth of mammals, reptiles and fishes. Among the marsupials (32), to which he has largely devoted himself, he has confirmed Kükenthal's conclusions, but he considers that the last incisor, in addition to the replacing premolar, is to be referred to the second dentition, a view which I have endeavoured to show is incorrect, as the tooth has the same relations as the anterior incisors, which are undoubted milk teeth (12). His work on the development of the human teeth (30, 31, 32) forms a most complete memoir of that subject, as also does that on *Didelphys* (32).

In his description of the dentition of the wombat (33) Röse figures what he considers to be a rudimentary milk

dentition succeeded by a permanent set of prismatic teeth. This, I think, is not the natural explanation of his own facts. He depicts five incisors on either side, above and below, but of the upper ones two are small and calcified and obviously from his figure represent the same tooth in two generations, this is i3 or 4, so we see that one incisor has been lost from the upper jaw, probably i3, the remaining three incisors represent those of the typical diprotodonts of which No. 1 probably is the persistent tooth; below we have five incisors, i1, 2 and 4 being vestigial and calcified, while i3 and 5 are well developed, the former persisting in the adult. There is not the slightest reason for supposing that these larger teeth are not true milk teeth. This explanation brings the wombat into harmony with the other marsupials and especially the *macropididæ*.

The third important contributor is Leche (34) and his work covers a wider range among the mammalia. While agreeing with the last two authors in the main, he believes that the milk dentition is in every respect older than the replacing one. His researches in the marsupials include a most interesting and new discovery in *Myrmecobius* of a number of small calcified teeth representing an earlier dentition than the milk set. This I have verified myself in the genus named and probably also in *Phascologale;* in order to distinguish the series from the milk set I shall for the present speak of it as the *premilk* dentition. This discovery relegates the milk dentition to a second and the replacing teeth of the higher mammals to a third generation of teeth.

The animal of whose dentition Leche has published the most detailed account is the hedgehog, in which he has discovered a very curious condition, for it appears that quite a number of the milk teeth persist in the adult dentition, *viz.* :—

$$\frac{\text{di3, dpm2, m 1-3}}{\text{di3, dc, dpm3, m 1-3.}}$$

This, if true, would rather strengthen the time-honoured view that the insectivora are very primitive mammals.

Both Leche (34) and Kükenthal (35) in the seal, and Röse (31) in man, have come to the conclusion that there

are traces of a third set of teeth succeeding the replacing set, so that together with the premilk series we appear to have in mammals traces of four dentitions, *viz.* :—

1st, or premilk dentition—minute calcified teeth never functional, present in *Myrmecobius*.[1]

2nd, or milk dentition—generally functional, the permanent dentition of marsupials and cetacea, more or less temporary in the higher mammals.

3rd, or replacing dentition—functional in most mammals, rudimentary in marsupials and cetacea.

4th dentition (?)—rudimentary in *Phoca* (?), occasionally functional in man (?).

While Leche maintains the view that the molars belong to the milk dentition and regards them as simple teeth, both Kukenthal and Röse consider that they are formed by the fusion of a number of distinct conical reptilian teeth. This idea is not a new one, it having been suggested by Gervais (36), Gaudry (37) and Dybowski (38) and others to explain the structure of the elephant's and ungulate's molars, but Kükenthal was undoubtedly the first to apply it to all mammals. Röse has taken up this view very strongly, and he attempts to prove it by embryological evidence, especially by what he has observed in the chameleon (39), where the back teeth are each composed of three cones, which, according to him, arise independently of one another, this is true to a certain extent; but these cusps develop under a common enamel organ and there is no indication of their ever having possessed independent organs as would have been the case if they were distinct teeth, there being merely a differentiation of the cylindrical enamel epithelium over each cusp, which Röse considers sufficient evidence in favour of his view. Kükenthal professes (35) to have seen in the walrus the fusion of two rudimentary molar germs into one, but unfortunately he does not figure this interesting find. He, however, puts forward this view of the molar tooth genesis as a theory drawn particularly from

[1] This premilk dentition is probably analogous to that seen by Leche in *Iguana* (40) and by Röse in the *crocodile* (41).

the consideration of reverse process seen to be taking place in the cetacea, and partially from palæontological evidence. He first (26) adduced *Triconodon* in proof of this view, regarding the molar tooth of that animal as a product of the fusion of three simple reptilian teeth; but in his later paper (29) he puts forward the view that the multituberculata are the forms which best demonstrate this point, and regards the three longitudinal rows of cusps seen in the multituberculate molar as indicative of the fusion of three distinct tooth generations, each consisting of a number of similar teeth. In the molar of the higher mammals he sees only two tooth generations represented, *viz.*, the milk and replacing set. This last condition is exemplified in the porpoise, in which he believes a fusion takes place between the two dentitions (28, p. 411, fig. 89), but the facts which he there describes appear rather indicative of the formation of a cusp by outgrowth from a simple conical tooth with far less effort than is required to see in them the fusion of two distinct dentitions. His belief that the "anlage" of the would-be successional molar becomes fused with that of the milk dentition will not hold for all mammals, for if the lingual continuation of the dental lamina (35, fig. 20, f. 2c, p. iv.) represents the anlage of the replacing teeth that structure can be seen in some mammals to remain quite distinct from the adult molar and in the end to gradually disintegrate, as the growth energy is abstracted from it by the larger and earlier developed tooth.

We find then that at present sufficient developmental evidence is not forthcoming to justify the conclusion that the mammalian molars are formed by the fusion of distinct teeth. With regard to the palæontological evidence, that is by no means so conclusive as Kükenthal seems to suggest, for the majority of observers in this branch of the study, and notably Osborn (43) and Schlosser (44), maintain that the tritubercular tooth is the primitive mammalian type and that it is to be derived from the simple reptilian cone, not by fusion with two other teeth but by the development of accessory cusps upon outgrowths of the pulp of the simple tooth. The steps in this evolution they exemplify by such forms as *Dromotherium* and *Microconodon*

of the trias of North America, which may therefore be as old as the multituberculate *Tritylodon*, the molar of which Osborn hopes soon to prove to be itself a specialised derivative of the tritubercular type.

On the other hand, Forsyth Major, who has for years paid special attention to this subject (42), is strongly of opinion that the primitive mammalian molar was polybunous in character; and if this can be proved to be the case the coalescence theory will naturally remain the simplest and most natural explanation of the origin of this type of tooth from the reptilian cone.

Reconsideration of the above-cited facts leads us to the belief (i.) that the living mammalia show traces of from three to four distinct generations of teeth, and consequently (ii.) that they are potentially polyphyodont, (iii.) that the first set is vestigial and not functional in any living mammal, (iv.) that the second, which is so important in the lower mammals, is more or less replaced by the third in the higher forms, and (v.) that this third dentition remains dormant in the marsupials and cetacea.

The point requiring immediate and renewed investigation is clearly the relation and mode of origin of the molar teeth, but I do not think we shall be able to make much advance towards the further solution of the general problem by embryological so fully as by palæontological research. If we are to regard it as proved that the triconodont tooth of the reptiles is formed by the fusion of three distinct teeth, we may safely apply the coalescence theory to the mammalian molar, but it is not likely that the latter would retain any very distinct indications of its originally distinct elements, especially if, as seems probable, the mammalia inherited their triconodont tooth, ready formed from their reptilian ancestor, in which case the early stages in the development would probably by now have been suppressed and the whole genesis abbreviated.

In the Ritter lecture, delivered at Jena in 1892, by Kükenthal (29), some very interesting views were put forward as to the origin of the mammalia, with special reference to the dentition, which he would derive from some

lowly form of theromorphous reptile and not from the more specialised Theriodontia. It is quite possible that the latter and the Mammalia had a common ancestor; and I think it is not improbable that the teeth of that form instead of being simple cones might already show traces of heterodontism.

The process of evolution of the specialised heterodont dentition of the Mammalia, or of the Theriodontia, from the simple homodont and polyphyodont dentition of the lower Reptilia would, I think, necessarily cause a reduction in number of the successional sets of teeth, due to an enlargement of one set and a consequent abstraction of growth, energy and material from the underlying sets. This specialisation would not appear in the first generation of teeth, which must necessarily be of small size from its early development and consequent adaptation to the small jaw of the young animal, and which would moreover be required for temporary use, while the larger and more complicated dentition was developing. The increased size and specialisation of the second set of teeth might well abstract the growth energy from the succeeding third and fourth sets which will consequently become much retarded and eventually cease calcifying. We find such stages illustrated by *Parieasaurus*, where the first dentition has probably been shed, the second is functional and the third is becoming reduced, and in the theriodonts, where the second dentition is still more specialised, no traces of the development of a third set is known (50, 51). We may thus provisionally conclude that the earliest mammalia may have possessed only two calcified sets of teeth, one of these being very slightly developed and quite temporary; and this tending to be still more so as the descendants of these animals developed their larger and more important heterodont dentition earlier and earlier; the process of reduction would go on until this first (premilk) dentition became either quite suppressed, as it is in the majority of mammals, or so much reduced as to be only present in the fœtus and never cutting the gum as is the case in *Myrmecobius* and possibly *Phascologale*. One very important feature concerned in the suppression of this set of teeth in the early

mammalia must have been the development of the mammary glands, which by providing the young animal with food would do away with the function of these teeth, which were so necessary to the young reptile, who must feed himself as soon as born.

The phase in which the polyphyodont dentition was reduced to a single functional set (the milk dentition of the higher mammalia) is probably represented by the earlier mesozoic mammals, in which we have no indication of any tooth change.

As the mammalia became more advanced in their organisation this heterodont second dentition took a stronger hold and developed earlier, then the third set, which had perforce lain dormant, began to reappear. If we are to regard the tooth succeeding the fourth (third) premolar of the marsupials as a replacing tooth, which I have shown reasons to doubt, it would appear to have been the first of the third set to attain functional importance ; and in favour of this view we may note that this tooth is one which, owing to the late development of the molars, is primarily the most posterior cheek tooth, and is of great importance to the young animal and early becomes much worn and so needs replacing more than the anterior teeth. Thus in the marsupials we find the last vestiges of the first set of teeth (premilk dentition), then we have a well-developed functional set, the second or milk dentition, under which in the embryo we find traces of a complete set of germs of the replacing or third dentition, the one replacing tooth being doubtfully referred to this set.

In the Insectivora we find the next stage in the development of the third set of teeth, for in the hedgehog replacing teeth are developed to the following—

$$\frac{i1,\ i2,\ C,\ pm3,\ pm4.}{i2,\qquad\quad pm4.}$$

the rest of the dentition consisting of persistent milk teeth.

In the majority of mammals replacing teeth of the third set are developed to all the incisors, the canines and the three posterior premolars, only a few like *Hyrax* developing a successor to the first premolar which in other cases is a persistent milk tooth.

If we do not regard the molar teeth as representing a fusion of several dentitions as advanced by Röse and Kükenthal, to which dentition are they to be relegated? Leche, Beauregard and Owen have considered them as belonging to the milk or second dentition, while I have tried to show that they belong to the third or replacing set. Owing to their late development and position in the jaw these teeth are much specialised, and they rarely show the slightest trace of any additional dentitions; but such structures have been observed both preceding and succeeding these teeth. Thus we find traces of three out of the four dentitions present for one tooth, and the whole question then turns on the point as to which set has been suppressed; if it is the first then the molars belong to the third replacing set, as Lataste, Magitot and I have suggested; if, on the other hand, it is the fourth dentition which is wanting, then Leche is right in supposing the molars to belong to the milk or second set.

The whole process of the first appearance of the molars is so involved owing to the loss of connection between the dental lamina and the gum in the region of their development that it seems very doubtful if we shall find any very distinct traces of additional preceding or succeeding teeth.

Bateson has recently described (45) a large and varied number of abnormalities affecting teeth. Many of these are simple sports or teratological cases, of which it is very difficult to offer any reasonable explanation; but, on the other hand, I see no reason to doubt, as he does, that the majority of those cases where additional teeth are present may be explained by the supposed increased development of some pre-existing tooth germ in the fœtus, especially as we now know of so many cases where these vestigial germs do exist (9, 12, 15, 27, 32, 33, 34, 48), and as these can in most instances be identified with definite teeth in the generalised mammalian dentition, I maintain that we are perfectly justified in trying to determine by comparison the individual homologies of these additional teeth, and further that they are often of great importance, as shown by Thomas in *Phascologale* (10). Bateson's comparison be-

tween the three normal and four abnormal premolars of *Ateles* (49) and the three sides of an equilateral triangle and the four sides of a square appears to me a little fanciful and premature, as I think it almost certain that when we examine the development of the teeth in that form we shall find that the germs of four premolars are invariably laid down, and that a definite one (retained in this abnormal specimen) always degenerates.

BIBLIOGRAPHY.

(1) F. CUVIER. *Des Dents des Mammiferes.* Paris, 1825.
(2) OWEN. *Odontology.* London, 1840-45.
(3) OWEN. *Todd's Cyclop. Anat.*, iv.
(4) OWEN. *Comp. Anat. and Phys. Verts.*, iii., 1868.
(5) OWEN. *Brit. Ass. Rep.*, 1848, p. 93.
(6) FLOWER. *Jour. Anat. and Phys.*, iii., 1869.
(7) FLOWER. *Phil. Trans.*, 1867.
(8) HUXLEY. *Proc. Zool. Soc.*, 1880.
(9) HUXLEY. *Hunterian Lecture.*
(10) THOMAS. *Phil. Trans.*, 1887.
(11) COPE. *Amer. Nat.*, 1887.
(12) WOODWARD. *Proc. Zool. Soc.*, 1892, 1893.
(13) BAUME. *Entwicklgs. des Gebisses.* Leipzig, 1882.
(14) THOMAS. *Proc. Roy. Soc.*, 1889-90.
(15) POUCHET and CHABRY. *Jour. Anat. Phys.* Paris, 1884.
(16) POULTON. *Proc. Roy. Soc.*, 1888.
(17) THOMAS. *Proc. Roy. Soc.*, 1889.
(18) STEWART. *Q. J. Micro. Sci.*
(19) RÖSE. *Anat. Anz.*, vii., 1892.
(20) LATASTE. (Six papers), *C. R. Soc. Biol.* (8), v., 1888.
(21) MAGITOT. *C. R. Soc. Biol.* (8), v., 1888.
(22) BEAUREGARD. *C. R. Soc. Biol.* (8), v., 1888.
(23) TOMES. *Manual of Dental Anatomy.*
(24) TOMES. *Q. J. Micro. Sci.*, xiv.
(25) FLOWER. *Proc. Zool. Soc.*, 1868.
(26) KÜKENTHAL. *Anat. Anz.* (13), vi., 1891; *Ann. Mag. N. H.*, 1892.
(27) KÜKENTHAL. *Anat. Anz.* (23), vi., 1891, and *Ann. Mag. N. H.*, 1892.
(28) KÜKENTHAL. *Denkschriften d. Med-Natuwis. Gesellsch.* Jena, 1893.
(29) KÜKENTHAL. *Biol. Centralb.*, xii., 1892; *Ann. Mag. N. H.*, 1892.

(30) RÖSE. *Verh. Anat. Gess.*, 1891.
(31) RÖSE. *Archiv Mikr. Anat.*, xxxviii.
(32) RÖSE. Various papers in *Anat. Anz.*, 1892-93.
(33) RÖSE. *S. B. Preus. Akad. d. Wiss.*, 1893.
(34) LECHE. *Morph. Jahrb.*, 1892 and 1893.
(35) KÜKENTHAL. *Jen. Zeit. f. Naturwis.*, xxviii.
(36) GERVAIS. *Mammiferes*, 1855.
(37) GAUDRY. *Enchainements du Monde Animal*, vol. iii., 1878.
(38) DYBOWSKI. *Verhand. d. K. R. Zool. bot. gesellch.* Wien, 1889.
(39) RÖSE. *Anat. Anz.*, viii., 1893.
(40) LECHE. *Anat. Anz.*, viii., 1893.
(41) RÖSE. *Schwalk's Morph. Arbeit*, 1893.
(42) FORSYTH MAJOR. *Proc. Zool. Soc.*, 1893, and *Nature*, vol. l., p. 101, 1894.
(43) OSBORN. *Anat. Anz.*, vii., 1892; and *Amer. Jour. Sci.*, xlvi., 1893.
(44) SCHLOSSER. *Biol. Centralb.*, x., 1890-91.
(45) BATESON. *Materials for the Study of Variation*, 1894.
(46) KRAUS. *Archiv f. Naturges*, 1862.
(47) LANKESTER and MOSELEY. *Journ. Anat. Phys.* London, iii., 1868.
(48) FREUND. *Archiv f. Mikr. Anat.*, 1892.
(49) BATESON. *Proc. Zool. Soc.*, 1892.
(50) SEELEY. *Proc. Roy. Soc.*, 1888.
(51) OWEN. *Quart. Jour. Geol. Soc.*, vol. xxxvii.

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ENUMERATION OF TITLES OF CHEMICAL PAPERS APPEARING IN MAY, 1894.[1]

American Chemical Journal.

Vol. xvi. No. 5. (May, 1894.)

Wood, R. W., The Affinity-Constants of Weak Acids and the Hydrolysis of Salts (pp. 313-326). *Kastle, J. H.*, The Color of Salts in Solution (pp. 326-340). *Phillips, F. C.*, Researches upon the Phenomena of Oxidation and Chemical Properties of Gases (pp. 340-366). *Jones, W.*, A Reduction-Product of Orthosulphobenzoic Chloride (pp. 366-370). *Lengfeld, F.*, and *Stieglitz, J.*, On Nitrogen Halogen Compounds (pp. 370-372). *Smith, W. R.*, On the Addition-Products of the Aromatic Isocyanides (pp. 372-393).

[1 It is proposed to continue this list for each month.—ED.]

The Analyst.

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Richmond, H. D., Some frequently-neglected Errors of Analysis (pp. 99-102). *Voelcker, J. A.*, The Occurrence of a Poisonous Leguminous Seed in Indian Peas (pp. 102-107). *Voelcker, J. A.*, Analyses of Waters from Wells in close proximity to Churchyards (pp. 107-109).

Journal of the Chemical Society.

Vol. lxv. No. 378. (May, 1894.)

Armstrong, H. E., Presidential Address.

Journal of the Society of Chemical Industry.

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Lovibond, J. W., Colorimetric Analysis, or Colour as a Means of Quantitative Estimation (pp. 308-318). *Young, W. C.*, The Natural Diminution of the Dissolved Organic Matter in the Water of Rivers (pp. 318-322). *Louis, H.*, Note on an Improved Specific Gravity Bottle (pp. 322-323). *Prentice, Manning*, Note on an Apparatus for the Continuous Production of Nitric Acid (pp. 323-324). *Platten, F.*, Modification of Ferric Chloride Distillation Process for Estimation of Arsenic in Copper (pp. 324-326). *De Mosenthal, H.*, The Treatment of Gold Ore at the Witwatersrandt (Transvaal) Goldfields (pp. 326-340). *Naylor, W.*, Comparative Results of some Modern Systems of Sewage Treatment (pp. 340-345). *Hummel, J. J.*, and *Perkin, A. G.*, The Tinctorial Properties of some Indian Dyestuffs. I. (pp. 346-354). *Cross, C. F.*, and *Bevan, E. J.*, The Theory of Dyeing (pp. 354-356). *Liechti, L.*, and *Hummel, J. J.*, On the Mordanting of Wool with Chromium. IV. (pp. 356-367). *Readman, J. B.*, The Effect of the Saline Constituents of Water on the Character of Beer (pp. 367-375). *Readman, J. B.*, A Useful Electric Furnace for Laboratory Work (pp. 375-376).

Philosophical Magazine and Journal of Science.

Vol. xxxvii. No. 229. (June, 1894.)

Lea, Carey M., A New Method of Determining the Relative Affinities of Certain Acids (pp. 557-564).

Chemical News and Journal of Physical Science.

Vol. lxix. No. 1797. (4th May, 1894.)

Phipson, T. L., On the Nature of Nitrogen (p. 207). *Liversidge, A.*, Gold Moiré-Métallique (p. 210). *Aslanoglon, P. L.*, Sea Water as a Chemical and Mechanical Depolarising Agent for Primary Batteries (pp. 210-211).

Vol. lxix. No. 1798. (11th May, 1894.)

Koninck, L. L. de, The Detection of Ammonia by Nessler's Solution (pp. 220-222).

Vol. lxix. No. 1799. (18th May, 1894.)

Darling, C. H., Action of Chlorine in presence of Sulphuric Acid (p. 232). *Paxton, H. D.,* Determination of Glycerin in Wine (p. 235). *Richmond, H. D.,* The Determination of the Strength of Sulphuric Acid (p. 236).

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7me série. Tome ii. (June, 1894.)

Moureu, G., Contribution à l'étude de l'acide acrylique et de ses dérivés (pp. 145-212). *Ouvrard, L.,* Combinaisons des sulfures de phosphore, d'arsenic et d'antimoine avec les halogènes (pp. 212-251). *Hugounenq, L.,* Recherches chimiques sur le liquide de la périostite albumineuse (pp. 256-270). *Minguin,* Étude de quelques dérivés du camphre cyané et de l'éther camphocarbonique (pp. 270-388).

Bulletin de la Société Chimique de Paris.

3e série. Tomes xi.-xii. No. 10. (20th May, 1894.)

Tanret, C., Réclamation au sujet de la pseudo-pelletiérine (p. 422). *Lepierre, C.,* Sur le poids atomique du thalliun (p. 423). *Sendfrens, J. B.,* Sur un cas singulier de précipitation métallique (pp. 424-426). *Guerbet,* Préparation de l'acide camphorique (pp. 426-434). *Barillé, A.,* Dosage de l'azote nitrique dans les eaux à l'état de bioxyde d'azote (pp. 434-436). *Combes, A.,* Sur quelques points de stéreochimie, response à M. Bouveault (pp. 436-439). *Franck, L.,* Action de l'aluminium sur le carbone et ses composés (pp. 439-446). *De Coninck, O.,* Rectification (p. 446). *Maquenne, L.,* Sur un nouveau baromètre de laboratoire (pp. 447-448).

Bulletin de l'Académie Royale des Sciences de Belgique.

Tome xxvii. No. 4. (1st June, 1894.)

Henry, L., Sur les hydrates des alkyl-amines (pp. 448-474).

Comptes Rendus hebdomadaires des séances de l'Académie des Sciences.

Tome cxviii. No. 19. (7th May, 1894.)

Berthelot, M., Recherches sur les gaz isomériques avec le propylène et sur leurs sulfates (pp. 1009-1013). *Brunhes, J.*, et *Dussy, J.*, Sur les variations de viscosité que présente le soufre fondu (pp. 1045-1046). *Cazeneuve, P.*, Sur des laques bleues dérivées de la dibromogallanilide et sur quelques réactions bleues des polyphénols (pp. 1046-1048). *Barral, Et.*, Sur un nouveau chlorure de carbone, le bichlorure de benzène hexachloré (p. 1049). *Barbier, Ph.*, et *Bouveault, L.*, Sur l'aldéhyde de l'essence de lémon grass (pp. 1050-1052). *Schloesing, Th., fils*, Sur la fabrication industrielle de produits riches en nicotine (pp. 1053-1055). *Petit, P.*, Sur l'oxydation des moûts de bière (pp. 1055-1057). *Chabrié, C.*, Recherches sur les transformations chimiques de la substance fondamentale du cartilage pendant l'ossification normale (pp. 1057-1060).

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Journal de Pharmacie (Anvers).

50me Année. (May, 1894.)

Arctowski, H., Faits relatifs aux propriétés du sulfure de carbone (pp. 169-175). *Plater-Syberg*, Nouveau procédé de fabrication de l'acide acétique et oxalique (pp. 175-176). *Denigès, G.*, Méthode générale pour le dosage volumétrique de l'argent sous une forme quelconque (pp. 176-181).

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Claisen., L., Beiträge zur Kenntniss der Pyrazolreihe (pp. 261-274). *Claisen, L.*, und *Roosen, P.*, I. Ueber die Einwirkung des Phenylhydrazins auf Oxymethylenaceton und auf Acetonoxalsäure (pp. 274-296); II. Ueber einige Sulfophenyl und Oxyphenylpyrazole (pp. 296-302). *Wallach, O.*, Zur Kenntniss der Terpene und der ätherischen Oele (28 Abhandlung); Ueber das Verhalten der Oxime cyclischer Ketone und die Ueberführung von Terpenderivaten in aliphatische Verbindungen von gleicher Anzahl der Kohlenstoffatome (pp. 302-329). *Schunck, E.*, und *Marchlewski, L.*, Zur Chemie des Chlorophylls (pp. 329-346). *Schunck, E.*, und *Marchlewski, L.*, Ueber die Einwirkung von Brom auf Datiscetin (pp. 346-349). *Schunck, E.*, und *Marchlewski, L.*, Studien über einige natürliche Zuckerarten. I. (pp. 349-359). *Platner, W.*, Ueber Benzophenonoxim aus Bisnitrosylbenzhydryl (pp. 359-373). *Seekamp, W.*, Ueber die Zersetzung der Weinsäure und Citronensäure durch das Sonnenlicht (pp. 373-375). *Schiff, Hugo*, und *Ostrogovich, A.*, Einige Reactionen des Orthotolidins (pp. 375-379).

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Zeitschrift für Analytische Chemie.

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Zeitschrift für Anorganische Chemie.

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Phillips, F. C., Untersuchungen über die chemischen Eigenschaften von Gasen. I. Erscheinungen bei der Oxydation von Wasserstoff und Kohlenwasserstoffen (pp. 213-228). II. Qualitative Reaktionem (pp. 229-255). *Arctowski, H.*, Ueber einige Eigenschaften des Schwefelkohlenstoffes (pp. 255-260). *Arctowski, H.*, Mitteilungen über Löslichkeitsverhältnisse. I. (pp. 260-268). *Gooch, F. A.*, und *Hodge, B.*, Nachweis und Abscheidung des Arsens bei Gegenwart von Antimon und Zinn (pp. 268-273). *Friedheim, Carl*, Beiträge zur Kenntniss der komplexen Säuren. X. (pp. 273-303). *Jannasch, P.*, Ueber die Bestimmung des Schwefels in Sulfiden, sowie über die gleichzeitige Ermittelung ihres Arsengehaltes. IV. (pp. 303-310). *von Woyczynski Casimir*, Ueber die künstliche Darstellung der dem Apatit und der Thomasschlacke analog Zusammengesetzten Baryum— und Strontiumverbindungen (pp. 310-312). *Wells, H. L.*, und *Penfield, S. L.*, Ueber Thalliumtrijodid und seine Beziehung zu den Trijodiden der Alkalimetalle (pp. 312-317). *Retgers, J. W.*, Ueber das gelbe Arsen (pp. 317-321). *Jannasch, P.*, und *Locke, J.*, Chemische Untersuchung des Topases (pp. 321-326).

Zeitschrift für Physikalische Chemie.

Band xiv. Heft 1. (22nd May, 1894.)

Retgers, J. W., Beiträge zur Kenntniss des Isomorphismus (pp. 1-53). *Cohen, E.*, Die Bestimmung von Umwandlungspunkten auf elektrischem wege und die elektromotorische Kraft bei chemischer Zersetzung (pp. 53-93). *Nickel, E.*, Ueber graphochemisches Rechnen. Teil VIII.: Zur Graphochemie der stickstoffhaltigen Verbindungen der Formel $C_n H_m N_p$ (pp. 93-105). *Paul, Th.*, Untersuchungen über fraktionierte Fällung (pp. 105-124). *Deventer van, Ch. M.*, und *Cohen, E.*, Ueber Salzbildung in alkoholischer Lösung (pp. 124-129). *Buckingham, E.*, Ueber einige Fluoreszenzerscheinungen (pp. 129-149). *Trevor, J. E.*, und *Kortright, F. L.*, Reaktionsgeschwindigkeit und Siedepunkt (pp. 149-151). *Natanson, L.*, Thermodynamische Deutung des Maxwellschen Gesetzes (pp. 151-155). *Nernst, W.*, Zur Dissociation des Wassers (pp. 155-157), *Lehmann, O.*, Ueber Sedimentation und

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Zeitschrift für Physiologische Chemie.

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Journal für Praktische Chemie.

Band xlix. Nos. 10, 11. (21st May, 1894.)

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